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CHEMICAL PROCESSING OF STRUCTURAL CERAMICS AND COMPOSITES

Final Report

September 1988

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Ultra-fine, ultra-pure and stoichiometric powders of mullite ($3Al_2O_3 \cdot 2SiO_2$), spinel ($MgO \cdot Al_2O_3$) and cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) were successfully synthesized through the hydrolytic and thermal decomposition of multicomponent metal alkoxides. Sol-gel processing studies of $MgAl_2O_4$ spinel demonstrated the potential for forming transparent spinel ceramics. Transparent sols were obtained with controlled hydrolysis of the double alkoxide solution. The spinel gel retained its optical transparency after 1000°C heat treatment. Sol-gel processing studies of cordierite showed that multicomponent silicate could be fabricated through sol-gel processing. The importance of drying conditions, calcination and sintering temperatures of the gels were enumerated.

Silicon oxynitride (Si_2ON_2) preceramic polymers were successfully synthesized by reacting polysilazane and polysiloxane in both "in-situ" and "graft" methods. The pyrolysis of the hybrid polymer in flowing NH_3 at 800°C yielded 86% Si_2ON_2 and a trace cf

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carbon. This Si_2ON_2 powder was hot-pressed in full density at 1700°C. The potential applications of the hybrid polymer were demonstrated as a thin film coating and ceramic-ceramic composite matrix. Si-Al-O-N precursor polymers were synthesized by reacting organosilicon polymers and aluminum alkoxides. The yield of ceramic powder, pyrolyzed at 800°C in NH_3 and subsequent heat-treatment at 1620°C in argon, was about 85%. However, the resulting phases were mullite and a trace of alumina. The nitrogen containing phase remained in an amorphous form.

FOREWORD

This report was prepared by the Materials Research Division of the Universal Energy Systems, Inc., Dayton, Ohio under Air Force Contract F49620-85-C-0118. Dr. D. R. Ulrich of the Air Force Office of Scientific Research, Chemical and Atmospheric Science, Bolling AFB, Washington, D.C., was the Government Program Manager. The research reported herein covered the period 15 July 1985 through 15 September 1988.

The scientific contributions were made by Drs. T. Mah and Y. F. Yu, Ms. L. P. Boothe, Mr. J. M. Battison and Ms. S. Heng. The authors would like to acknowledge Mr. E. E. Hermes for valuable discussions and Mrs. H. L. Henrich for preparation of this report.

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Section I

INTRODUCTION

Chemical processing of ceramics has drawn considerable attention in recent years. This is mainly due to the realization that by controlling the structures, surfaces, and interfaces of materials at the molecular level, to achieve high performance ceramic components or devices, in the earliest stages of processing.

Universal Energy Systems, Inc. (UES), has conducted exploratory, experimental, and analytical investigations on the following subjects through chemical processing: i) synthesis and application of organosilicon polymers, ii) sol-gel processing of multi-component metal oxide systems, and iii) chemical processing of high temperature oxide superconductors. Summarized are major findings and the most recent and relevant additional results have also been included in this report. In addition to these, a number of publications have resulted from these investigations and are attached in the Appendix.

Section II

SUMMARY OF RESEARCH

Research activities followed in this program are outlined below. Detailed results on each subject can be found in the Appendix.

In the area of organosilicon polymer processing the following advances were made:

1) Synthesis of polysilazane and polysiloxane, and subsequent reactions, by the "in situ" and "graft" methods, to synthesize a silicon oxynitride (Si_2ON_2) preceramic polymer.

2) Successful conversion of the above hybrid polymer into Si_2ON_2 powder.

3) Densification studies and subsequent microstructural analysis of Si_2ON_2.

4) Feasibility studies of thin film coating by the spin-on method using the above hybrid polymer.

5) Limited, exploratory studies of ceramic-ceramic composite fabrication using the above hybrid polymer as the matrix precursor.

6) Exploratory synthesis studies of Si-Al-O-N precursor polymers by reacting organosilicon polymers and aluminum alkoxides.

The following advances were made in metal alkoxides and sol-gel processing area:

1) Systematic studies on hydrolytic and thermal decomposition of multicomponent metal alkoxides to produce mullite ($3Al_2O_3 \cdot 2SiO_2$), spinel ($MgO \cdot Al_2O_3$), and cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) powders were carried out. The effects of pH, time, and temperature on the hydrolysis process were studied and related to the final powder morphologies.

2) Sol-gel processing of transparent spinel and cordierite was carried out. Studied were the effects of solvent, molar ratio of water to metal alkoxides, reaction temperature, catalyst, and drying control chemical additives in the preparation. Drying conditions and densification procedures in the gelling process and the effects of calcination and sintering temperatures on the crystallization and densification of cordierite were studied.

In high temperature superconductor research, preliminary experiments were initiated to develop chemical processing routes for synthesizing superconducting materials. Studies of various combinations of alkoxides, acetates and hydroxides of yttrium, barium and copper were considered as potential precursor candidate materials. Preliminary experiments on mixed metal acetate systems showed the potential to fabricate melt-spinnable superconducting fiber precursors. Ultra-fine, ultra-pure superconducting single-phase oxide powder syntheses, using hydrolytic decomposition processing of mixed metal-organics, were studied.

Section III

ADDITIONAL INVESTIGATIONS

SOL-GEL PROCESSING OF CORDIERITE ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$)

Introduction

The objective of this research was to produce a homogeneous ternary silicate gel using mixed metal alkoxides. The alkoxide process was chosen because it has been shown to be a low temperature chemical process which offers the potential for control over purity, homogeneity and stoichiometry.[1] Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) was the ternary silicate chosen for this research.

The electronic packing industry also has an interest in low temperature processing to produce multi-layered substrates that can be co-fired with good electrical conductors such as Cu, Au and Pd-Ag.[2] Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) has the potential to be an alternative electronic packing material to alumina. It has a lower dielectric constant and thermal expansion coefficient.[2] Cordierite also has the potential for lower sintering and densification temperatures than α-alumina. In addition to being a potential electronic packing material, cordierite, if made transparent, has the potential to be to used in UV transmitted pieces such as radomes, etc.

In this research, the study of the sol to gel transition of the cordierite mixed metal alkoxide system was qualitatively carried out. Additionally, the densification behavior of the dry gels was studied.

Experimental

The precursor for the gels was made through the alkoxide process. The magnesium ethoxide was prepared by reacting pure magnesium metal with ethyl alcohol in the presence of a catalyst (Eq. 1). Similarly, pure aluminum metal was reacted with isopropyl alcohol to produce the aluminum isopropoxide (Eq. 2). Silicon alkoxide was purchased (Alfa Products) since it is relatively stable.

$$Mg + 2C_2H_5OH \text{ ---> } Mg(OC_2H_5)_2 + 1/2H_2 \quad (1)$$

$$Al + 3C_3H_7OH \text{ ---> } Al(OC_3H_7)_3 + 1/2H_2 \quad (2)$$

The magnesium and aluminum alkoxides were mixed together and heated until they had completely reacted. Once the magnesium/aluminum complex had formed, the excess solvents were removed by vacuum drying. This formed a stock alkoxide complex from which all subsequent gels were made. The dried magnesium/aluminum alkoxide was weighed out in calculated portions and redissolved in ethyl alcohol. An appropriate amount of tetraethoxysilane (TEOS) was added to form a final product of stoichiometric cordierite (2:2:5).

The cordierite alkoxide was hydrolyzed under various conditions and allowed to gel. The resulting gels were aged and dried. On selected gel conditions, the effect of ageing and drying of the gels was studied. Various analyses were carried out on the dried gels, including DTA/TGA, X-Ray Diffraction (XRD), SEM and chemical analysis. Based upon the DTA/TGA results, various heat treatments were performed for densification.

Results

The various hydrolysis conditions and time to gelation are summarized in Table 1.

TABLE 1. Time to Gelation.

TIME TO GELATION

HYDROLYSIS CONDITION	WATER/MAS MOLE RATIO			
	36 : 1	**20 : 1**	**16 : 1**	**5 : 1**
ROOM TEMP	13 DAYS	13 DAYS	20 DAYS	27 DAYS
40 C BATH	7 DAYS	13 DAYS	17 DAYS	26 DAYS
60 C BATH	3 DAYS	10 DAYS	11 DAYS	26 DAYS
PTLY HYDRO TEOS/WATER	---	11 DAYS	---	27 DAYS
PTLY HYDRO TEOS/ACID	---	20 DAYS	---	25 DAYS
PTLY HYDRO TEOS/60 C	---	12 DAYS	---	25 DAYS
PTLY HYDRO TEOS/60 C/ACID	---	12 DAYS	---	24 DAYS
PTLY HYDRO TEOS/ACID/DCCA	---	12 DAYS	---	24 DAYS

The hydrolysis conditions were room temperature, 40°C, 60°C and the partial hydrolysis of TEOS under various conditions. In addition to the various hydrolysis conditions, the water to magnesium aluminum silicate (MAS) alkoxide mole ratios were also varied. The ratios chosen were 36:1 due to the 36 (OR) groups in the MAS alkoxide; 20:1 because 20 (OR) groups are associated with the TEOS; 16:1 for the 16 (OR) groups associated with the $MgAl_2$ complex; and 5:1, this is equivalent to a 1:1 mole ratio of water to TEOS.

To summarize Table 1 results, it appeared that the gelation time increased with decreasing mole ratio of water to MAS alkoxide. It could be explained that the more water present, the easier it is for a hydroxide to form, and thus, form a colloidal gel. Even though the time to gelation decreased with increasing hydrolysis temperature in some cases, the overall appearance of the gels themselves, within a particular water to MAS mole ratio, did not vary appreciably.

In addition to the hydrolysis temperature, partial hydrolysis of TEOS was carried out for the 20:1 and the 5:1 water to MAS alkoxide mole ratios. The conditions included partial hydrolysis at room temperature and 60°C; and hydrolyzed with water, 0.1 M nitric acid, and 0.1 M nitric acid with a drying control chemical additive (DCCA) formamide. The results appeared to show no overall difference in the gelation time within a given water to MAS mole ratio. There did not appear to be any difference in the overall appearance of the gels due to partial hydrolysis either. Therefore, the partial hydrolysis route was not pursued any further.

The chemical analysis of the dried gels with 16:1 water to MAS alkoxide mole ratio showed the gels to be 2:2:5 mole ratio of MAS. It has been reported that TEOS requires a catalyst, either base or acid, in order to be completely hydrolyzed. However, the results from the chemical analysis indicates that the TEOS used in this study will completely hydrolyze without the presence of any catalyst.

After examining the dry gels, the 16:1 mole ratio of water to MAS showed better gels under the ageing and drying conditions used. In this research a better gel was defined as a gel having fewer cracks and somewhat transparent after drying. Further studies were then carried out using only the 16:1 mole ratio.

A large batch of the MAS alkoxide was hydrolyzed at room temperature with water to MAS being 16:1. This large batch was separated into several small flasks and allowed to gel, which took approximately two weeks to occur. The effect of ageing on the gels was studied. These gels were aged 1 day, 1 week, 2 weeks, and 3 weeks, and then dried.

During the drying cycle, it appeared that gels aged for less time had a tendency to crack earlier than gels aged longer. This was true to a point, if a gel was aged too long, longer than 3 to 4 weeks, the gel would crack before the drying cycle started. Although the gels would crack earlier with less ageing, DTA analysis, performed later on the dried gels, showed no difference due to the ageing of the gels. Under the experimental conditions employed in the research, it appeared that an ageing of 2 to 3 weeks resulted in the best gel in terms of large, crack-free pieces.

The drying schedule was such that the temperature was increased every two or three days from 50°C, to 70°C, to 85°C and finally to 105°C. After being dried at 105°C, the following analyses were carried out; DTA/TGA, XRD, SEM and chemical analysis.

A typical DTA/TGA curve is shown in Figure 1. The analysis was performed on powdered gels; starting from room temperature to 1300°C, at a 5°C/minute heating rate. The results showed an endothermic reaction around 200°C, followed by two exothermic peaks ending around 800°C. These peaks were accompanied with a significant weight loss, leveling off around 800°C. Detailed reactions occurring below 800°C is not clear at present. Further research is planned, in collaboration with AFWAL/MLLM scientists, to carry out in-situ mass spectrometry and DTA analysis.

The study was concentrated on the exotherms at ∿ 980°C and at ∿ 1080°C . To determine what was occurring at these two exotherms, systematic DTA runs were made stopping just before and after each peak. XRD and SEM analyses were then carried out on each of the samples run in the DTA. The temperatures chosen were 920°C, 1000°C, 1100°C, and 1300°C.

A typical amorphous XRD pattern was observed on the 920°C sample (Figure 2). For the 1000°C sample, high quartz structure MAS ($MgAl_2Si_3O_{10}$, JCPDS No. 25-511) was the only phase present. Thus, the exothermic peak at 980°C was due to crystallization of high-quartz structure MAS. In the XRD data for the 1100°C sample, both high-quartz structure MAS and low-cordierite (JCPDS No. 13-294) were present, indicating a phase transformation had taken place. Upon examining the DTA curve closer, it was determined that the 1100°C sample was on the down slope of the exotherm peak at 1080°C. Therefore an additional DTA run was made taking the sample to 1200°C. In this XRD pattern, only low-cordierite was present, which was the same as the 1300°C run. These results indicate that the exotherm at 1080°C was due to the phase transformation from high-quartz MAS to low-cordierite.

The SEM micrographs of the samples after DTA runs are shown in Figure 3. Since the micrographs were taken from loosely packed powders from the DTA runs, any speculations about the microstructure development were precluded. However, the micrographs do show a densification occurring between the 920°C and the 1000°C samples. The micrograph at 920°C is very similar to that of the crushed gels at room temperature. However, the micrograph of the 1000°C sample shows a more rounded nature of particles, as well as, some necking between particles (partial sintering). The XRD analysis indicated that crystallization also was taking place. This may indicate that the 980°C exotherm on the DTA curve was due to both densification and crystallization.

Using the results from the DTA curve, heat treatment conditions were scheduled to study the densification behavior of the gels. The temperatures chosen were 960°C, 1015°C, 1100°C and 1300°C.

The first set of samples were slowly taken up to 1015°C and held for 64 hours. This resulted in foamed MAS gels. From this it was determined that the gels needed to go through a calcining step, before heat treatment, in order to densify the gels. However, the foamed gels brought up an aspect of the gels that had not been considered -- that is, as refractory thermal insulating materials for electronics and space applications.

A set of gels were then calcined at 600°C for 16 hours. Select pieces of the gels were heated to 960°C for 64 hours. The gels foamed again, but not as much as the first time. According to the TGA curve, the weight loss appeared to end between 700°C to 800°C.

Another set of gels were calcined around 770°C and then heat treated to 1200°C for 64 hours. Although the gels did not foam as the previous runs, they still did not densify. The gels had expanded in size, but the large pore on the outside surface, present in the other runs, was not evident. Some pieces had the appearance of styrofoam. The same was evident when the gels were heated to 1300°C for 64 hours.

At this time a more concentrated effort was placed on the densification of the gels, or to determine at which temperature the "foaming" was taking place. The calcination temperature was raised to 800°C and was heated at 1°C/minute from 200°C to 800°C, and held for 16 hours. The gels were then slow cooled to avoid any thermal shock. All previously calcined gels were still very black after calcination, indicating that the organic groups had not been completely removed. However, the gels calcined to 800°C had an amber translucent appearance with several cracks in the pieces. These calcined gels were subjected to further heat treatment at 900°C. Several pieces were heated to 800°C rapidly and then heated to 900°C at a rate of 1°C/minute. The gels were held at 900°C for two hours and then slowly cooled. The result was a gel that had held its original shape and that was transparent.

Several more pieces of calcined gels were then heated to 1000°C. Included with these gels was a gel piece that had only been calcined to 770°C. The gels were heated to 800°C rapidly and then heated at 1°C/minute to 1000°C. Again, the gels were held for two hours and then slowly cooled. This heat treatment resulted in the 800°C gels retaining their original shape but becoming white opaque. The 770°C gel reacted as it had done in the previous runs, expanding and having a styrofoam appearance. This gave evidence that the reason the previously calcined gels had foamed was because the gels had not seen the optimum calcination temperature, and thus causing the evolution of the remaining organic groups at the higher temperatures. In addition, it demonstrates that the optimum calcination window is small, considering there is only 30°C between the last two calcination temperatures.

Additional gels were heat treated in the same manner to 1100°C, 1200°C and 1300°C. In all cases the results were the same, gels that retained their original shapes, dense and were white in color.

Conclusion

It has been shown that a ternary silicate gel could be made through the mixed metal alkoxide route. In addition, under the conditions that were employed in this study, a molar ratio of 16:1, water/MAS, provided the better looking gels. Although the ageing of the gels played into the crack development, as seen from the DTA analysis, it did not appear to have an effect of sintering behavior or crystallization.

From the XRD and DTA data, it was shown that initial crystallization to high-quartz structure MAS and sintering occurs below 1000°C with transformation to low-cordierite occurring below 1100°C.

The heat treatment brought out some interesting results. First, a foamed material can be made from the gels that could have the potential to be used as thermal insulation. Second, there is a small optimum calcination window to which the gels must be heated in order to form a dense gel. Third, a transparent, amorphous gel can be produced under the proper conditions. This could potentially find applications in UV transmitted pieces, if the internal stress cracking can be alleviated.

REFERENCES

1. K. S. Mazdiyasni, "Chemical Synthesis of Single and Mixed Phase Oxide Ceramics," Mater. Res. Soc. Symp. Proc., 32, 175-186 (1984).

2. C. Gensse and U. Chowdry, "Non-Conventional Route to Glass-Ceramics for Electronic Packaging," Mater. Res. Soc. Symp. Proc., 72, 297-307 (1986).

3. R. K. Iler, The Chemistry of Silica, (John Wiley, NY) 1979.

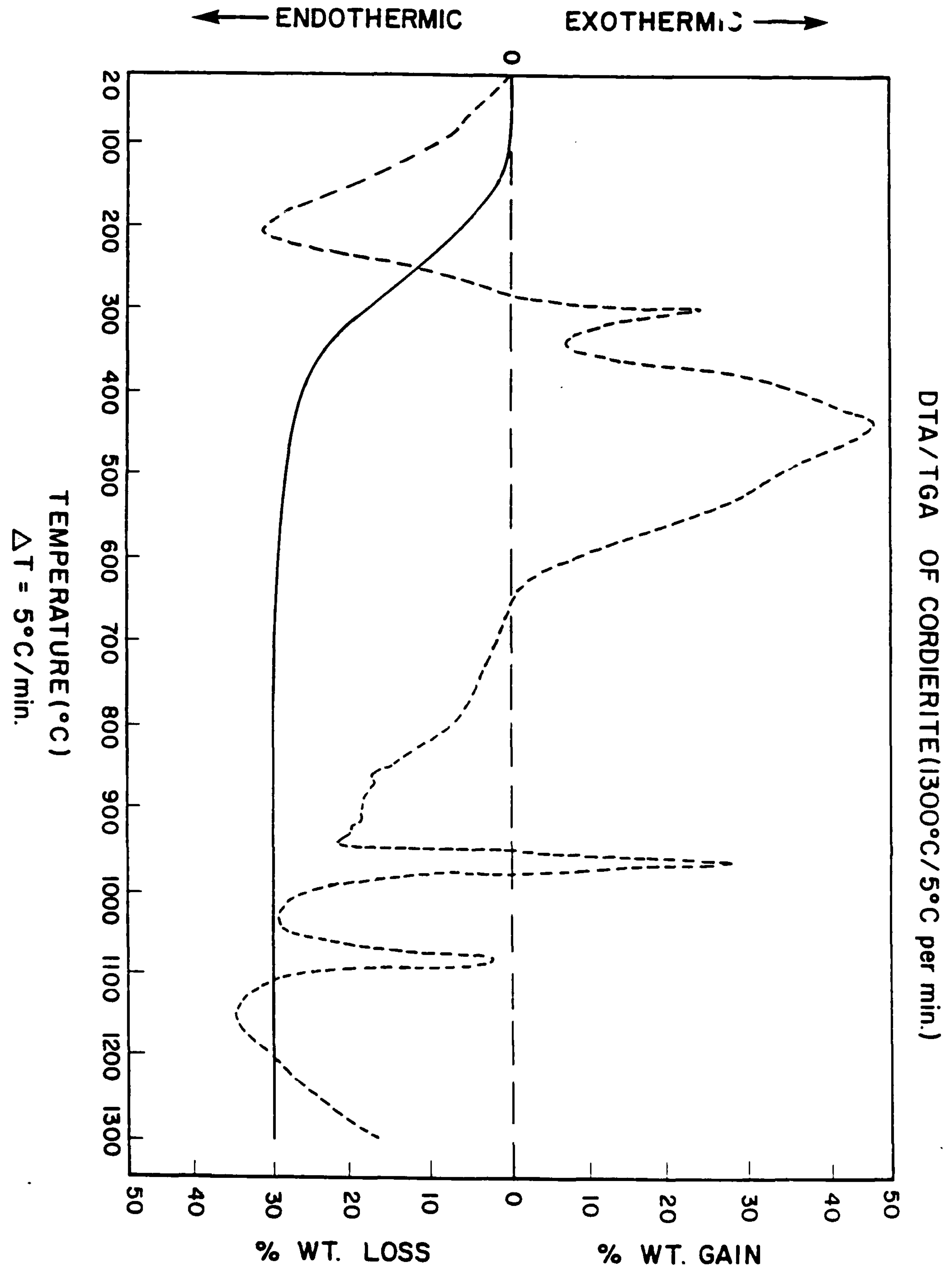
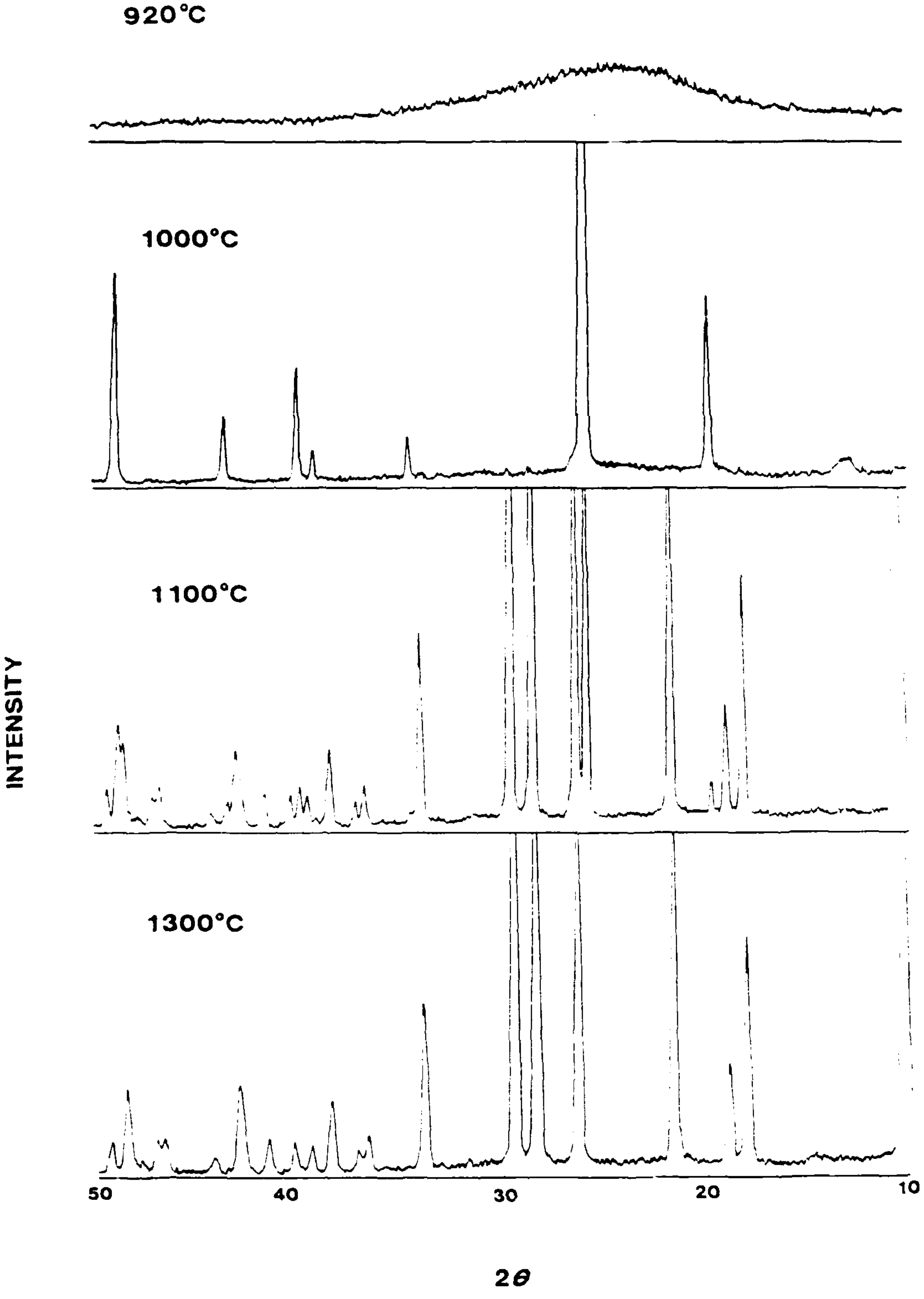

DTA/TGA OF CORDIERITE(1300°C/5°C per min.)
ENDOTHERMIC
EXOTHERMIC
0
20
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
TEMPERATURE(°C)
ΔT = 5°C/min.
50
40
30
20
10
0
10
20
30
40
50
% WT. LOSS
% WT. GAIN

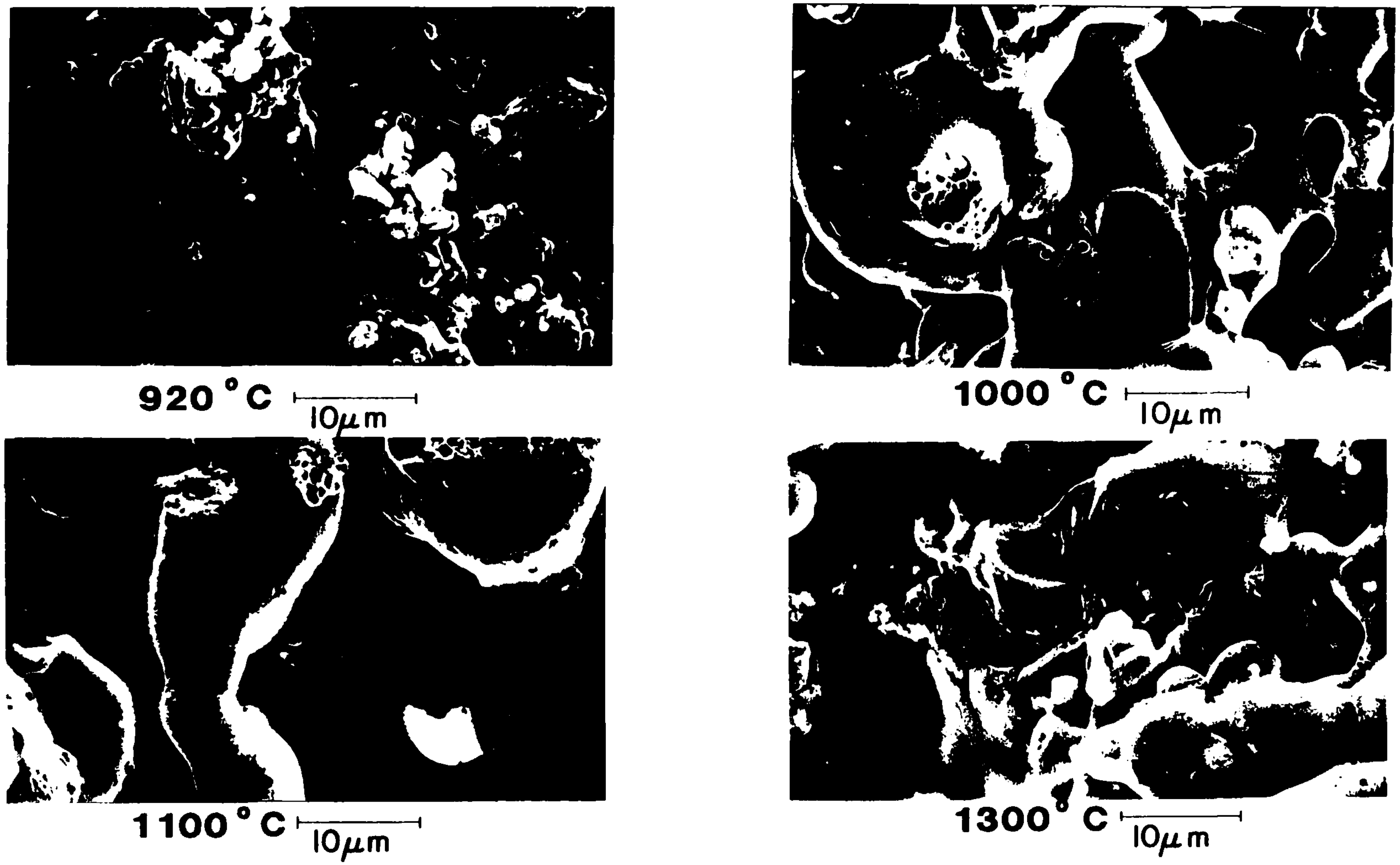
Figure 1.



X-RAY DIFFRACTION PATTERNS OF CORDIERITE GELS

AFTER VARIOUS HEAT TREATMENTS

Figure 2.



920 °C 10μm

1000 °C 10μm

1100 °C 10μm

1300 °C 10μm

SEM MICROGRAPHS OF POWDERED GELS AFTER
VARIOUS DTA / TGA RUNS

Figure 3.

APPENDIX

CONTENTS OF APPENDIX

1. Si-O-N CERAMICS FROM ORGANOSILICON POLYMERS, published in Better Ceramics through Chemistry II, Edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich, Elsevier, NY, 559 (1986).

2. CERAMIC POWDERS FROM METAL-ORGANIC PRECURSORS, published in Advances in Ceramics, The American Ceramic Society, 1987.

3. SILICON OXYNITRIDE AND Si-Al-O-N CERAMICS FROM ORGANOSILICON POLYMERS, published in the Proceedings of the Third International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites, San Diego, CA, CA, 28, 389 (1987).

4. SOL-GEL PROCESSING OF TRANSPARENT $MgAl_2O_4$, published in the Proceedings of the 1988 Spring Meeting, Reno, NV, April 5-9, 1988, Materials Research Society, Better Ceramics through Chemistry III.

5. SOL-GEL SYNTHESIS OF HIGH T_c SUPERCONDUCTORS, Senior Thesis, Wright State University, Dayton, Ohio.

Si-O-N CERAMICS FROM ORGANOSILICON POLYMERS

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ABSTRACT

The preparation of new, hybrid pre-ceramic organosilicon polymers are described. These hybrid polymers were prepared by reactions of polysilazanes and polysiloxanes. Ceramic materials containing Si-O-N were obtained with high yields ($\sim$ 80%) by pyrolyzing these new polymers at low temperatures ($<$ 800°C). A wide range of chemical compositions and properties can be obtained by using different ratios of polysilazanes and polysiloxanes. Microstructural characterization and densification studies of these ceramic materials are present.

INTRODUCTION

In recent years, great interest has developed in silicon-containing pre-ceramic polymers whose pyrolysis provides silicon containing ceramics such as silicon carbide, silicon nitride, silicon carbonitride, silicon oxynitride, etc. [1]. The use of these organosilicon polymers provides a unique approach for preparation of numerous ceramic materials in all their useful forms (powders, coatings, fibers, foams, or monoliths) [2].

In the present work, new organosilicon polymers were prepared by reacting easily prepared polysilazane and Si-H containing polysiloxanes. Pyrolysis of these new hybrid organosilicon polymers under flowing NH_3 gas produced high purity silicon oxynitride Si_2ON_2 in good yield. Densification studies on the pyrolyzed powder were performed using the hot-press. The dense monolithic bodies were characterized using x-ray diffraction (XRD) analysis and scanning electron microscopy (SEM).

BACKGROUND

Silicon oxynitride is a good refractory material of highly desirable properties for the fabrication of parts such as nozzles, turbine blades, or other structural elements subjected to high temperatures [3,4]. Si_2ON_2 is stable up to 1550°C in an inert atmosphere. When exposed to air at temperatures in the range of 1400 to 1750°C, Si_2ON_2 has an oxidation resistance superior to that of silicon nitride.

Despite the close structural simulations between Si_3N_4 and Si_2ON_2, ceramics based on Si_2ON_2 has received little attention. The lack of an economical and reproducible method to produce pure Si_2ON_2 is the reason for this. Washburn [5] has shown that the nitridation of a mixture of silica and elemental silicon in a controlled atmosphere containing nitrogen and oxygen with metal oxide (CaO, BaO, MgO, etc.) as the catalyst will yield Si_2ON_2.

$$3Si + SiO_2 + 2N_2 \xrightarrow[1450°C]{Catalyst} 2Si_2ON_2 \qquad (1)$$

However, in addition to the formation of Si_2ON_2 ($\sim$ 75%), a considerable amount of silicon nitride ($\sim$ 15%) was formed and some unreacted SiO_2 was also found.

HYBRID POLYMER SYNTHESIS [6]

Experiments were carried out with polysiloxane $[CH_3Si(H)O]_m$ prepared using conditions under which the yield of the cyclic oligomers ($m = 4,5,6$) is maximized

$$CH_3SiHCl_2 + H_2O \xrightarrow{CH_2Cl_2} [CH_3Si(H)O]_m + 2HCl \qquad (2)$$

The ammnolysis of CH_3SiHCl_2 in THF produced a mobile oil in higher than 80% yield. Spectroscopic data suggested that this colorless oil had a mostly cyclic $\{CH_3SiHNH\}_n$ structure [7].

$$CH_3SiHCl_2 + NH_3 \xrightarrow[0°C]{THF} [CH_3SiHNH]_n + NH_4Cl \qquad (3)$$

In one approach, the "graft" method, a reactive polymeric alkali metal silylamide was prepared by using $[CH_3SiHNH]_n$ and catalytic quantities of KH in THF. To this living polymer solution the $[CH_3Si(H)O]_m$ oligomers were added slowly and the active metal species in the solution were quenched with CH_3I. The average molecular weight of the hybrid polymer prepared from 1:1 weight ratio of silazane to siloxane is ∿ 1700 g/mol, much higher than its starting materials (∿ 300 g/mol for both silazane and siloxane). This polymer has excellent solubility in hexane, benzene, and THF.

$$(CH_3SiHNH)_n \xrightarrow[THF]{KH} [(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]_{n'}$$

$$\downarrow [CH_3Si(H)O]_m$$

$$\downarrow CH_3I$$

"Graft" Hybrid Polymer (4)

Using an alternative synthesis method of $[CH_3SiHNH]/[CH_3Si(H)O]$ combined polymers, the polysilylamide was generated "<u>in-situ</u>" in the presence of $[CH_3Si(H)O]_m$.

$$[CH_3SiHNH]_n + [CH_3Si(H)O]_m \xrightarrow[THF]{KH} \xrightarrow{CH_3I} \text{"In-Situ" Polymer} \qquad (5)$$

The combined polymer prepared by the "in-situ" and "graft" polymer methods differed in some ways. The TGA curves of the "graft" polymer and the "in-situ" polymer differ and the ceramic products, when pyrolyzed under a stream of NH_3 gas, are different as well. Properties of some of the hybrid polymers synthesized are summarized in Table I.

CONVERSION OF POLYMER TO CERAMIC

When polymers with organic substituents on the Si atom are used to prepare ceramic materials, the products generally will contain carbon and silicon carbide if they are pyrolyzed in vacuum or inert atmospheres. However, when the pyrolysis is carried out in a stream of ammonia, the ceramic remains usually contains less than 0.5% carbon. One example of this process is pyrolyzed SiO_2-containing polycarbosilane fibers (cured precursor fiber of NICALON) under NH_3 to give silicon oxynitride fibers [8].

TABLE I. Properties of Hybrid Polymers

Hybrid Polymer	Yield(%)	Weight Ratio of Siloxane : Silazane	Synthesis Method	M.W.[a] (g/mol)	Appearance[b]
I	88	1:1	In-Situ	1670	White Solid
II	83	1:1	Graft	1700	White Solid
III	69	5:1	In-Situ	760	White Solid
IV	80	5:1	Graft	2400	White Solid

[a] Cryoscopic in Benzene Solution

[b] All four polymers are very soluble in hexane, benzene, and THF.

Pyrolysis of the hybrid polymers (Table I) to 1000°C under inert atmosphere gave black ceramics with good yields (Table II). More significantly, we have found that pyrolysis of these hybrid polymers, heated to 800°C in gaseous ammonia, provided white solids in high yields. Analysis confirmed that these white solids are silicon oxynitrides. These white ceramics contain little if any, carbon. Some preliminary weight loss versus temperature experiments, indicate the majority of reactions between polymer and NH_3 gas are most likely to occur around 600 to 700°C. It is suggested that at higher temperatures (> 400°C), the NH_3 molecules effect nucleophilic cleavage of the Si-C bonds present in the polymer and the methyl groups are lost as CH_4.

TABLE II. Conversion of Hybrid Polymers to Ceramic

Hybrid Polymers	TGA[a] Yield(%)	Ceramic[b] Yield(%) NH_3	Composition[c]	Carbon[c] (%)	Density[c] (g cm^{-3})
I	84	86	Si_2ON_2	0.15	2.48
II	78	78.5	Si_2ON_2 + β-Si_3N_4	0.48	2.66
III	61	82	Si_2ON_2 + SiO_2	0.13	Porous

[a] In argon, 10°C/min., 1000°C

[b] In NH_3, 100°C/hr., 800°C

[c] Hot-pressed sample, 1700°C

A ceramic pellet was prepared by charging the fine hybrid polymer powder I into a 3/4 in. in diameter stainless-steel die. The sample was pryolyzed in gaseous ammonia, heated to 800°C, and held at that temperature for one hour. The product was a coherent, round white ceramic pellet which had not cracked or bloated. The sample lost 14% of its original weight and the average diameter reduced to 9/16 in. The SEM micrograph of the fracture surface shows both dense and powdery agglomerated regions. The specimen was then heat-treated in argon at 1300°C for two hours. The SEM micrograph of the fracture surface are shown in Fig. 1. The picture shows that a certain degree of sintering had taken place during the 1300°C heat-treatment, however, it appears that a much higher temperature is needed to achieve appreciable densification. Hot-pressing was used to further heat-treat the material at higher temperatures and to obtain a fully dense body. The hybrid polymer I was first pyrolyzed in flowing NH_3 gas at 800°C to obtain the white ceramic powder, the powder was then ground slightly and loaded into a 1-in. in diameter graphite die. The final hot-pressing conditions were 1700°C, 2000 psi for 15 min. in nitrogen atmosphere. Figure 2 is a SEM micrograph of the fracture surface of the hot-pressed dense pellet. The micrographs revealed two microstructural features; (a) a very dense region, and (b) porosity nests which are associated with fine Si_2ON_2 grains and interconnecting pores. The average grain size appeared to be slightly less than one micrometer. The uniformity of the grain size implies homogeneous nucleation and growth process during crystallization from the amorphous state (800°C pyrolysis). The crystallization process of the hybrid polymer I derived silicon oxynitride obtained at 800 to 1700°C in NH_3 gas was examined by the XRD technique with monochromated Cukα radiation (result shown in Fig. 3). At lower temperatures, 800 and 1300°C, XRD patterns of the pyrolyzed samples shows only background diffraction, suggesting a complete amorphorus nature of the samples. This amorphorus character to XRD is not uncommon for ceramic materials derived from organosilicon polymers pyrolysis. The crystallization of Si_2ON_2 from the pyrolyzed specimen took place between 1300 and 1550°C. XRD patterns of the 1550 and 1700°C samples show strong peaks which can be easily assigned to silicon oxynitride diffractions.

Similar ceramic body fabrication experiments were carried out using the fine "graft" hybrid polymer II powder. A slightly brown and very dense ceramic pellet was obtained by hot-pressing the white ceramic powder at 1700°C, 2000 psi for 15 min. in nitrogen atmosphere. The surface XRD pattern of the pellet derived from polymer II, showed Si_2ON_2 diffractins and β-Si_3N_4 diffractions as the minor phase. This result indicates that even though hybrid polymers I and II were prepared from identical starting materials and pyrolyzed under the same condition, the ceramic products are not the same. In terms of Si_2ON_2 preparation, the "In-Situ" hybrid polymer I is a better pre-ceramic polymer than the "graft" hybrid polymer II. The surface XRD pattern of the hot-pressed pellet derive from the siloxane reached hybrid polymer III exhibited Si_2ON_2 diffractions and the expected SiO_2 broad peaks.

CONCLUSION

In this paper we have shown that pure silicon oxynitride can be prepared by pyrolysis of new hybrid organosilicon polymers in gaseous ammonia. The major advantage of this polymer pyrolysis route over conventional methods is that stoichiometric Si_2ON_2 can be obtained at low temperatures with high-purity and the absence of minor phases. Another advantage of this hybrid polymer system is the utilization of readily available and relatively cheap polysiloxane and polysilazane. The third advantage of this system is that the composition of hybrid polymers, as well as ceramic products, can be easily modified by adjusting the ratio of polysiloxane and polysilazane.

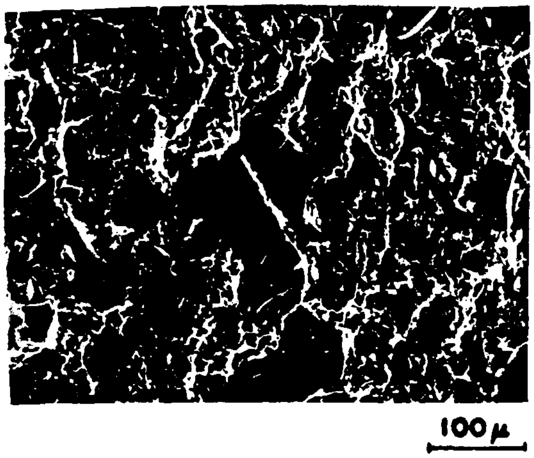

Figure 1. Sem Micrograph of Hybrid Polymer I Derived Ceramic at 1300°C in Argon.

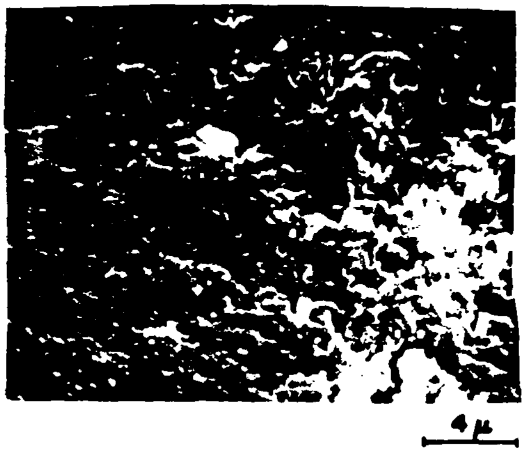

Figure 2. SEM Micrograph of Hybrid Polymer I Derived Ceramic at 1700°C Hot-Pressed.

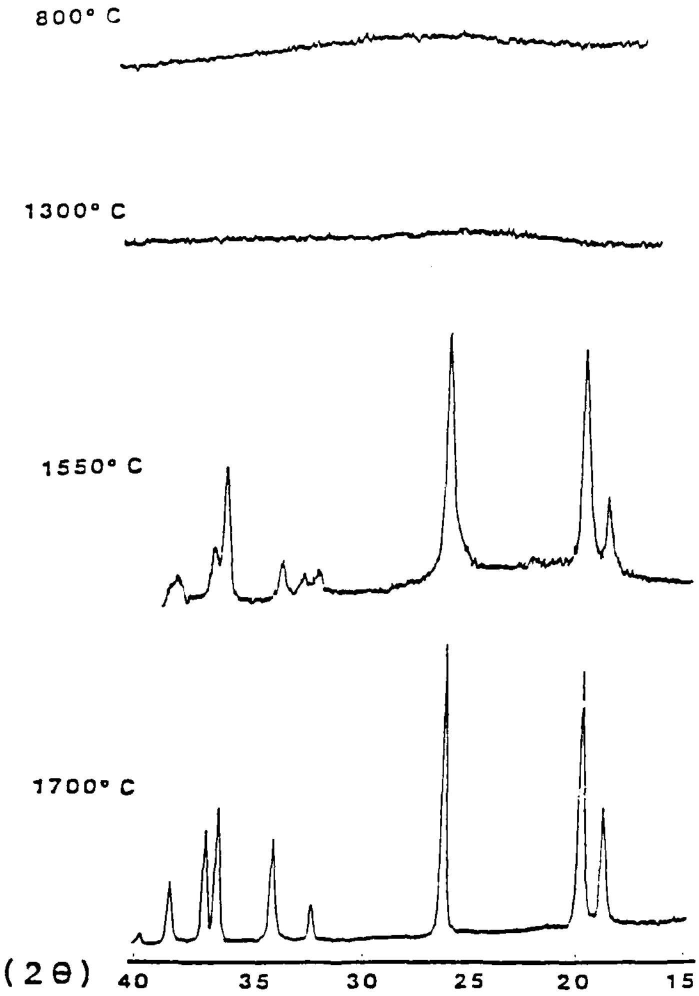

Figure 3. XRD Patterns of Hybrid Polymer Derived Si_2ON_2 at Different Temperatures.

ACKNOWLEDGEMENTS

This work was sponsored by the Air Force Office of Scientific Research (AFOSR) under Contract No. F49620-85-C-0118. The hybrid polymers used in this research were developed at MIT by Y. F. Yu with Professor D. Seyferth.

REFERENCES

1. D. R. Ulrich and L. L. Hench, Ultrastructure Processing of Ceramics, Glasses and Composites, (Wiley Interscience, NY, 1984) p. 5.
2. R. W. Rice, Bull. J. Am. Ceram. Soc. 62, 889, (1983).
3. "Engineering Property Data on Selected Ceramic," Vol. 1, Nitrides, MCIC-HB-07, Battelle Laboratories, Columbus, Ohio.
4. M. E. Washburn, Bull. J. Am. Ceram. Soc. 46, 667 (1967).
5. M. E. Washburn, U.S. Patent No. 3356513 (5 December 1967), U.S. Patent No. 3639101 (1 February 1972).
6. D. Seyferth and Y. F. Yu, and T. S. Targo, U.S. Patent Pending.
7. D. Seyferth and G. W. Wiseman, U.S. Patent No. 4482669 (13 November 1984).
8. K. Okamura, M. Sato, Y. Hasegawa, and T. Amano, Chem. Lett. 2059 (1984).

CERAMIC POWDERS FROM METAL-ORGANIC PRECURSORS

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ABSTRACT

Hydrolytic and thermal decomposition of multicomponent metal alkoxides were used to produce ultra-fine and ultra-high-purity oxide powders. The effect of pH, time, and temperatures on the hydrolysis of mullite precursor mixed alkoxides (TEOS and aluminum isopropoxide) were studied. The effect of pH on hydrolysis was significant due to the presence of TEOS. The resulting particle size and agglomeration were also affected by pH. The crystallization and growth of alkoxy-derived spinel were studied using XRD and TEM. Optically transparent spinel was produced by hot-pressing. Synthesis of cordierite, through a mixed alkoxide process, is described and its advantages over conventional glass frit methods are discussed.

INTRODUCTION

Hydrolytic and thermal decomposition of metal alkoxides have been used to prepare a wide variety of high-purity oxide powders.[1] Refractory oxides, with submicron particle size, can be prepared by a simple chemistry reaction to fulfill specific requirements which cannot be obtained readily by conventional ceramic processing methods.[2] When mixtures of alkoxides are hydrolyzed, the different hydrolysis rate of each individual alkoxide can cause complications, which may lead to microscopic inhomogeneities. If one species is hydrolyzed faster than the others, then differential precipitation will occur during hydrolysis, while the other species remain substantially unreacted. Silicon alkoxides are slow to hydrolyze in comparison to other alkoxides.[3] Therefore, if a solution of silicon and other alkoxides is prepared by physical mixing, a differential hydrolysis rate may prevent the formation of stoichiometric homogeneous powders.

The preparation of ultra-fine mullite, spinel, and cordierite powders by using multicomponent alkoxide systems will be reported. The model system chosen to study the temperature, reaction time, and pH effects upon mixed alkoxide hydrolysis was mullite ($3Al_2O_3 \cdot 2SiO_2$). The size and composition of ceramic powders obtained under different reaction conditions are also discussed.

EXPERIMENTAL

Synthesis of Metal Alkoxides

Tetraethyl orthosilicate (TEOS)* was used as-received without further purification. Aluminum trisisopropoxide was prepared from high-purity aluminum foil† and isopropyl alcohol using a small amount of $HgCl_2$ as a catalyst.[4] Magnesium bisethoxide was prepared by reaction of magnesium metal chips‡ with anhydrous ethyl alcohol in the presence of small amounts of HgI_2.[5]

$$Al + 3C_3H_7OH \xrightarrow[\Delta]{HgCl_2} Al(OC_3H_7)_3 + 3/2H_2\uparrow \qquad (1)$$

$$Mg + 2C_2H_5OH \xrightarrow[\Delta]{HgI_2} Mg(OC_2H_5)_2 + H_2\uparrow \qquad (2)$$

Synthesis of Ceramic Powders

Preparation of various metal alkoxides were performed under argon gas to avoid moisture. Transferring of metal alkoxides was accomplished by cannulation with a stainless-steel needle.

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* TEOS - 99% pure; Alfa Products, Danvers, MA.

† Aluminum Foil - 99.999% pure; Alfa Products, Danvers, MA.

‡ Magnesium - 99.99% pure; Alfa Products, Danvers, MA.

Mullite

Aluminum trisisopropoxide, $Al(OC_3H_7)_3$, in excess isopropyl alcohol, was added into a stoichiometric amount of TEOS. This mixed metal alkoxide solution was then used as a stock solution. Aliquots of the mixed alkoxide solution were withdrawn from the stock for each experiment. The alkoxide solutions were hydrolytically decomposed under various pH, temperature, and heating times using nitric acid and ammonium hydroxide as catalysts. The resulting hydroxy-aluminosilicate was dried by rotary evaporation under reduced pressure to remove excess solvent. The mixture was then refluxed with a deagglomerating agent and the excess adsorbed water was removed by distillation. The residual organic group was removed by calcination at 550°C for one hour.

Spinel

The two metal alkoxides, $Al(OC_3H_7)_3$ and $Mg(OC_2H_5)_2$, were mixed together, gently heated in isopropyl alcohol until $Mg(OC_2H_5)_2$ was completely reacted producing a clear solution, and then allowed to cool to room temperature. The solution was then slowly added into a mixture of 75% water and 25% methyl alcohol and stirred vigorously. The resulting milky slurry was dried by rotary evaporation under reduced pressure to remove the excess solvent. The mixture was then refluxed with the deagglomerating agent and the excess adsorbed water was removed by distillation. The residual organic group was removed by calcination at 550°C for one hour.

Cordierite

For cordierite preparation, mixed metal alkoxide of aluminum and magnesium was prepared by the same procedure as above. TEOS was added to the clear double alkoxide solution of $Mg(OC_2H_5)_2$ and $Al(OC_3H_7)_3$. This solution was then thoroughly mixed. Hydrolytic decomposition was accomplished by slowly adding the mixed alkoxide solution to a basic water-methyl alcohol (3:1) solution at pH=10, using ammonium hydroxide as the catalyst. The hydroxide slurry was then subjected to rotary evaporation to remove excess solvent. Deagglomeration and calcination processes were the same as described previously.

RESULTS AND DISCUSSION

Extensive studies of the hydrolysis and condensation conditions were conducted on mixed TEOS and $Al(OC_3H_7)_3$ alkoxides system. Due to the differences in the hydrolysis behavior of TEOS and $Al(OC_3H_7)_3$, attempts were made to study whether the two alkoxides could form a double alkoxide complex. The experiment was followed by IR measurements. A stoichiometric amount of TEOS was added to aluminum isopropoxide, refluxed for 48 hours, then the excess isopropyl alcohol was removed by distillation. No double alkoxide complex formation was evident by the IR spectrum of the reaction mixture. The mixture was further heated to 190°C, then refluxed at that temperature for two hours. The IR spectrum (Fig. 1) of the reaction mixture showed two new peaks at 895 cm^{-1} and 905 cm^{-1} which cannot be assigned to TEOS, $Al(OC_3H_7)$, or solvents. However, the IR spectrum of the distillate of the reaction mixture at

190°C shows absorption bands that can be assigned to TEOS. Therefore, for the hydrolysis study, the two alkoxide mixture was treated as unreacted, yet homogeneous.

The overall hydrolysis and condensation reactions of TEOS and $Al(OC_3H_7)$ may be described schematically as:[6]

$$6Al(OC_3H_7)_3 + 2Si(OC_2H_5)_4 + xH_2O \xrightarrow[\text{or } HNO_3]{NH_4OH} 6Al(OH)_3 \cdot 2Si(OH)_4 + \text{Alcohols} \qquad (3)$$

$$6Al(OH)_3 \cdot 2Si(OH)_4 \xrightarrow[\text{Calcination}]{550°C} 3Al_2O_3 \cdot 2SiO_2 \qquad (4)$$

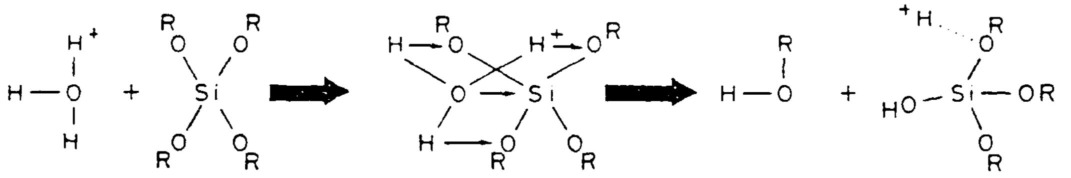
The above hydrolytic reaction is very sensitive to experimental conditions, such as the presence of acidic or basic catalysts, reaction temperature, and molar ratio of alkoxides to H_2O. Three critical experimental parameters, pH, temperature, and reaction time, which affected the rate of hydrolysis, were systematically studied. For all of the experiments, the volume ratio of 100 ml of mixed alkoxide solution to 500 ml of a H_2O/CH_3OH (3:1 ratio) solution was used. The results are summarized in Table I. To ensure reproducibility of each experiment, a large batch of mixed alkoxide solution was prepared in excess isopropyl alcohol and aliquots were withdrawn from this.

It was found that in an acidic environment (pH=2), the hydrolytic decomposition was completed within seven hours at room temperature. Stoichiometric mullite was the only product obtained as evidenced by both elemental analysis and an x-ray diffraction (XRD), Fig. 2. Under the alkaline condition (pH=10), the degree of hydrolytic decomposition was both time and temperature dependent. The TEOS was only partially hydrolyzed even after heating at 70°C for

20 hours. The oxide powder obtained was composed of 65% Al_2O_3 and 35% mullite. In the neutral condition, pH=6.5, the oxide powder obtained was mainly alumina. The degree of hydrolysis is only moderately affected by temperature and it is not affected by the reaction time. This result is consistent with our previous IR finding. Therefore, the hydrolytic decomposition of mixed TEOS and $Al(OC_3H_7)_3$ alkoxides is controlled mainly by the rate of TEOS decomposition, since $Al(OC_3H_7)_3$ can be readily hydrolyzed in water without any catalysts.

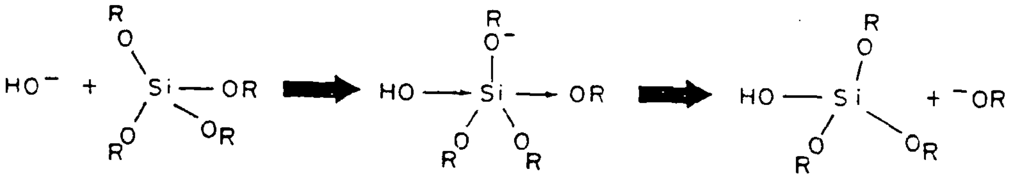
The difference between acid versus base catalyzed hydrolysis of mixed TEOS and $Al(OC_3H_7)_3$ can be accounted for by the different reaction mechanisms of TEOS hydrolysis.[7] Nucleophilic hydrolysis and condensation in alkaline solutions tend to produce highly crosslinked species, which may not be completely hydrolyzed. In contrast, in acidic solutions, the electrophilic reaction mechanism favors the production of weakly crosslinked species which tend to be completely hydrolyzed.[8]

Acid Catalyzed



(5)

Base Catalyzed



(6)

The specific surface area of the as-calcined mullite powder obtained from acidic hydrolysis condition is 197 m^2/g. Clusters of particles develop during concentration of the hydroxide slurry. These particles polymerize upon further drying, causing bound -OH groups in the clusters, thereby resulting in hard agglomerates instead of fine powder. Emission spectrographic analysis of the mullite powder showed no measurable impurities present. X-ray diffraction analysis exhibited a pure mullite diffraction pattern. Ultra-fine mullite powder, with a surface area of 416 m^2/g, can be obtained by hydrolytic decomposition of mixed TEOS and $Al(OC_3H_7)_3$ under an alkaline condition. A calibrated amount of TEOS needs to be added to compensate for the slow hydrolytic decomposition of TEOS under this condition.

Spinel powder was prepared by the hydrolytic decomposition of $Mg(OC_2H_5)_2$ and $Al(OC_3H_7)_3$. A double alkoxide, with Al-O-Mg linkage, can easily be prepared in solution.[9] The hydrolytic decomposition and calcination reactions are summarized in the following equations:

$$Mg(OR)_2 + 2Al(OR)_3 \longrightarrow Mg \cdot Al_2(OR)_8 \qquad (7)$$

$$Mg \cdot Al_2(OR)_8 + H_2O \longrightarrow Mg \cdot Al_2(OH)_8 + 8ROH \qquad (8)$$

$$Mg \cdot Al_2(OH)_8 \xrightarrow[\Delta]{} MgAl_2O_4 \qquad (9)$$

$$R = (CH_3)_2CH,\ C_2H_5,\ etc. \qquad (10)$$

The double alkoxide was readily hydrolyzed by water, without acid or base catalyst. No differential hydrolytic decomposition of mixed alkoxides was found in this system to hinder the formation of ultra-fine homogeneous spinel powder. The x-ray diffraction analysis (Fig. 3) of the ultra-fine powder obtained after calcination at 550°C shows amorphous characteristics. The powder was calcined at 1000°C for one hour and XRD analysis showed broad peaks of spinel. Distinct, sharp x-ray diffraction peaks of spinel can be observed after the powder was hot-pressed at 1550°C. Elemental analysis of the powder calcined at 550°C gave a 1:1 MgO to Al_2O_3 ratio. Emission spectrographic analysis of the as-calcined powder indicated no measurable impurities were present. Surface area of the as-calcined powder* was 260 m^2/g, which corresponds to an average particle size of 6.5 nm. The transmission electron micrograph (TEM) of the as-calcined powder (Fig. 4) showed the particle size to be in the order of 10 nm, which is in agreement with the calculated value. The oxide powder was further heat treated at 1000°C for one hour. The average particle size of the powder increased $\sim$ 30 nm, and the particles are faceted.

A typical hydrolytic decomposition process from mixed metal alkoxides, for the preparation of MAS (including cordierite) powder, is illustrated in Fig. 5. Submicron size stoichiometric cordierite powder can be easily prepared by a hydrolytic decomposition of the mixture $Mg(OC_2H_5)_2$, $Al(OC_3H_7)_3$, and TEOS under an acidic condition. However, if ultra-fine particle size is desirable, a calculated amount of TEOS can be added to obtain the stoichiometric composition under an alkaline hydrolytic decomposition condition.

* Leeds & Northrup Co., Microtrac Division, St. Petersburg, FL.

† SG266M Cordierite glass frit, Ferro Corp., Cleveland, OH 44101

The cordierite powder obtained through hydrolysis, using a base catalyst, was extremely fine and fluffy. A tap density of the powder was found to be 0.11 g/cc. The tap density of the commercially obtained[†] fritted glass was measured as 0.80 g/cc. Comparing the alkoxide derived powder to the fritted glass powder, the tap density was more than seven times smaller.

CONCLUSION

The alkoxy hydrolysis technique was used to prepare stoichiometric high-purity amorphous mullite, spinel, and cordierite powders at low temperature. The powder obtained through this technique produces ultra-fine particle sizes, which can be obtained without a milling process. Because no milling is required, the high-purity of the powder is maintained. Additionally, the ultra-fine particles lead to highly reactive powders. Because of the high reactivity of the powder, low processing temperatures can be achieved. By being able to process samples at low temperatures, low boiling elements can be retained. In addition to processing advantages, the composition homogeneity and composition flexibility can be achieved through the metal alkoxide method. Due to the fact that the alkoxides are mixed in the low viscosity liquid phase, a more complete and homogeneous mixing is realized. Furthermore, dopant addition can be easily carried out in the liquid phase, resulting in a composition that is flexible to the users need.

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REFERENCES

1. K. S. Mazdiyasni, "Powder Synthesis from Metal-Organic Precursors," Ceramics International 8, 42-56 (1982).

2. K. S. Mazdiyasni, "Chemical Synthesis of Single and Mixed Phase Oxide Ceramics," Better Ceramics through Chemistry, C. J. Brinker, D. E. Clark, and D. R. Ulrich, eds. (North-Holland, 1984) p. 175-186.

3. B. E. Yoldas, "Preparation of Glasses and Ceramics from Metal-Organic Compounds," J. Mater. Sci. 12, 1203-1208 (1977).

4. D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, Metal Alkoxides, (Academic Press, NY, 1978) p. 411.

5. H. Adkins and J. Cox, J. Amer. Chem. Soc. 60, 1151 (1938).

6. K. S. Mazdiyasni and L. M. Brown, "Synthesis and Mechanical Properties of Stoichiometric Aluminum Silicate (Mullite)," J. Amer. Ceram. Soc. 55, 548-552 (1972).

7. R. K. Iler, The Chemistry of Silica, (John Wiley, NY, 1979).

8. K. D. Keefer, "The Effect of Hydrolysis Conditions on the Structure and Growth of Silicate Polymers," Better Ceramics through Chemistry, C. J. Brinker, D. E. Clark, and D. R. Ulrich, eds. (North-Holland, 1984) p. 15.

9. S. Goviland, R. C. Mehrotra, Sym. React. Inorg. Metal-Org. Chem., 5. 267 (1975).

FIGURE CAPTIONS

Figure 1. IR Spectrum of Reaction Mixture $Al(OC_3H_7)_3$ and TEOS at 190°C.

Figure 2. X-Ray Diffraction of Metal Alkoxide Derived Mullite Powders at Various pH.

Figure 3. X-Ray Diffraction of Metal Alkoxide Derived Spinel Powder Processed at Different Temperatures.

Figure 4. Transmission Electron Micrographs of Dispersed Spinel Powder, Calcined at (a) 550°C and (b) 1000°C in Air for One Hour.

Figure 5. MAS (Cordierite) Powder Preparation from Mixed Metal Alkoxides.

Table I. Hydrolytic Decomposition of TEOS and $Al(OC_3H_7)_3$ under Various Experimental Conditions.

HYDROLYSIS CONDITION	TIME	TEMPERATURE	MOLAR RATIO OF Al_2O_3/SIO_2 FROM CHEMICAL ANALYSIS	XRD
ACIDIC pH=2	20 HOURS	RT	* * * *	100% MULLITE
		70°C	$3Al_2O_3$:$2SIO_2$	100% MULLITE
	7 HOURS	RT	* * * *	100% MULLITE
		70°C	* * * *	100% MULLITE
BASIC pH=10	20 HOURS	RT	$12Al_2O_3$:$1SIO_2$	~ 80% Al_2O_3 ~ 20% MULLITE
		70°C	$6Al_2O_3$:$1SIO_2$	~ 65% Al_2O_3 ~ 35% MULLITE
	7 HOURS	RT	* * * *	~ 85% Al_2O_3 ~ 15% MULLITE
		70°C	* * * *	~ 80% Al_2O_3 ~ 20% MULLITE
NEUTRAL pH=6.5	20 HOURS	RT	$49Al_2O_3$:$2SIO_2$	~ 90% Al_2O_3 ~ 10% MULLITE
		70°C	* * * *	~ 85% Al_2O_3 ~ 15% MULLITE
	7 HOURS	RT	* * * *	~ 90% Al_2O_3 ~ 10% MULLITE
		70°C	* * * *	~ 85% Al_2O_3 ~ 15% MULLITE

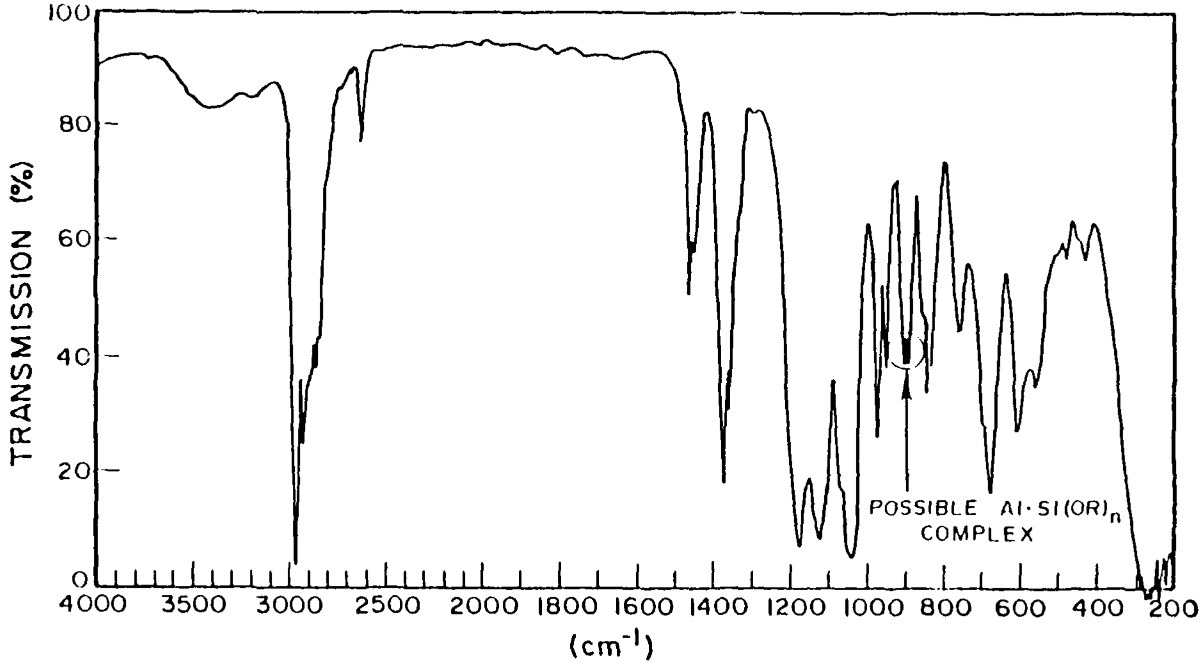

Figure 1. IR Spectrum of Reaction Mixture $Al(OC_3H_7)_3$ and TEOS at 190°C.

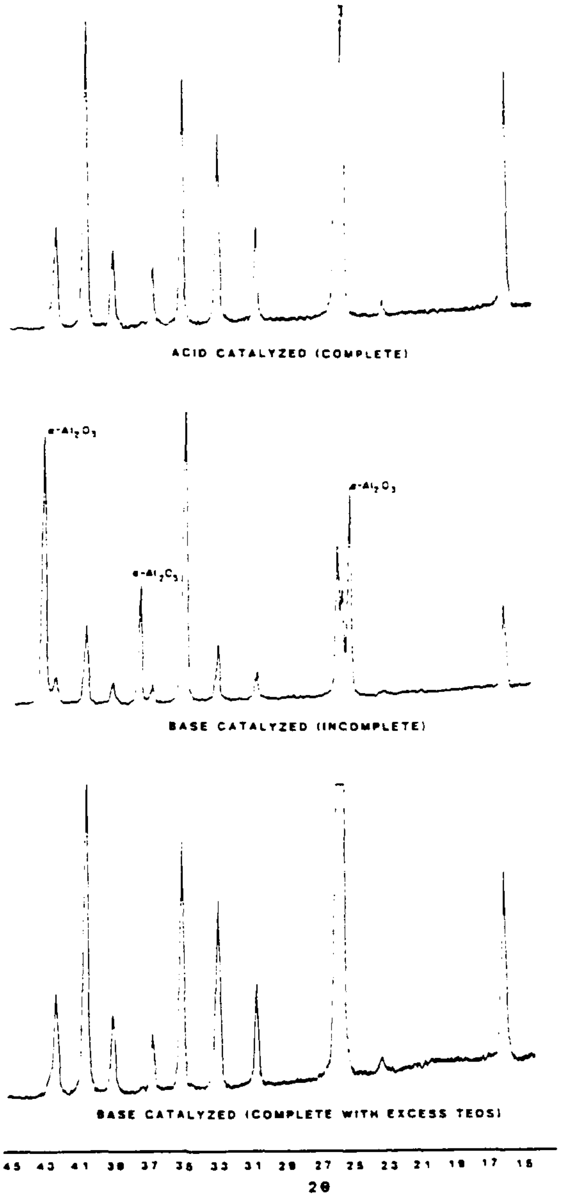

Figure 2. X-Ray Diffraction of Metal Alkoxide Derived Mullite Powders at Various pH.

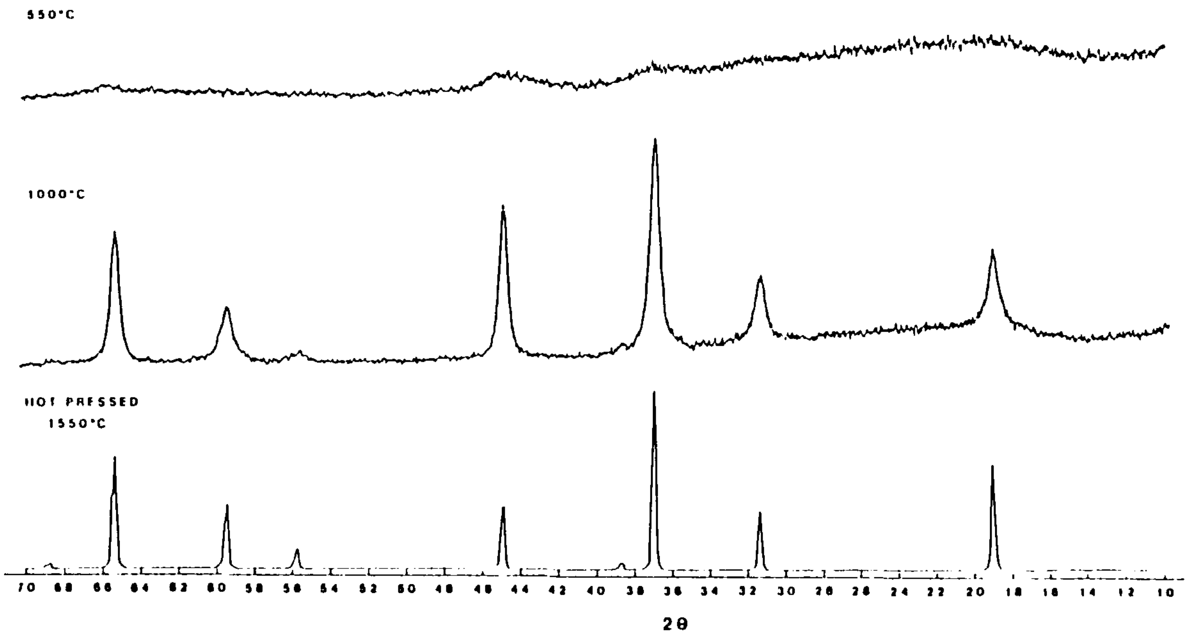

Figure 3. X-Ray Diffraction of Metal Alkoxide Derived Spinel Powder Processed at Different Temperatures.

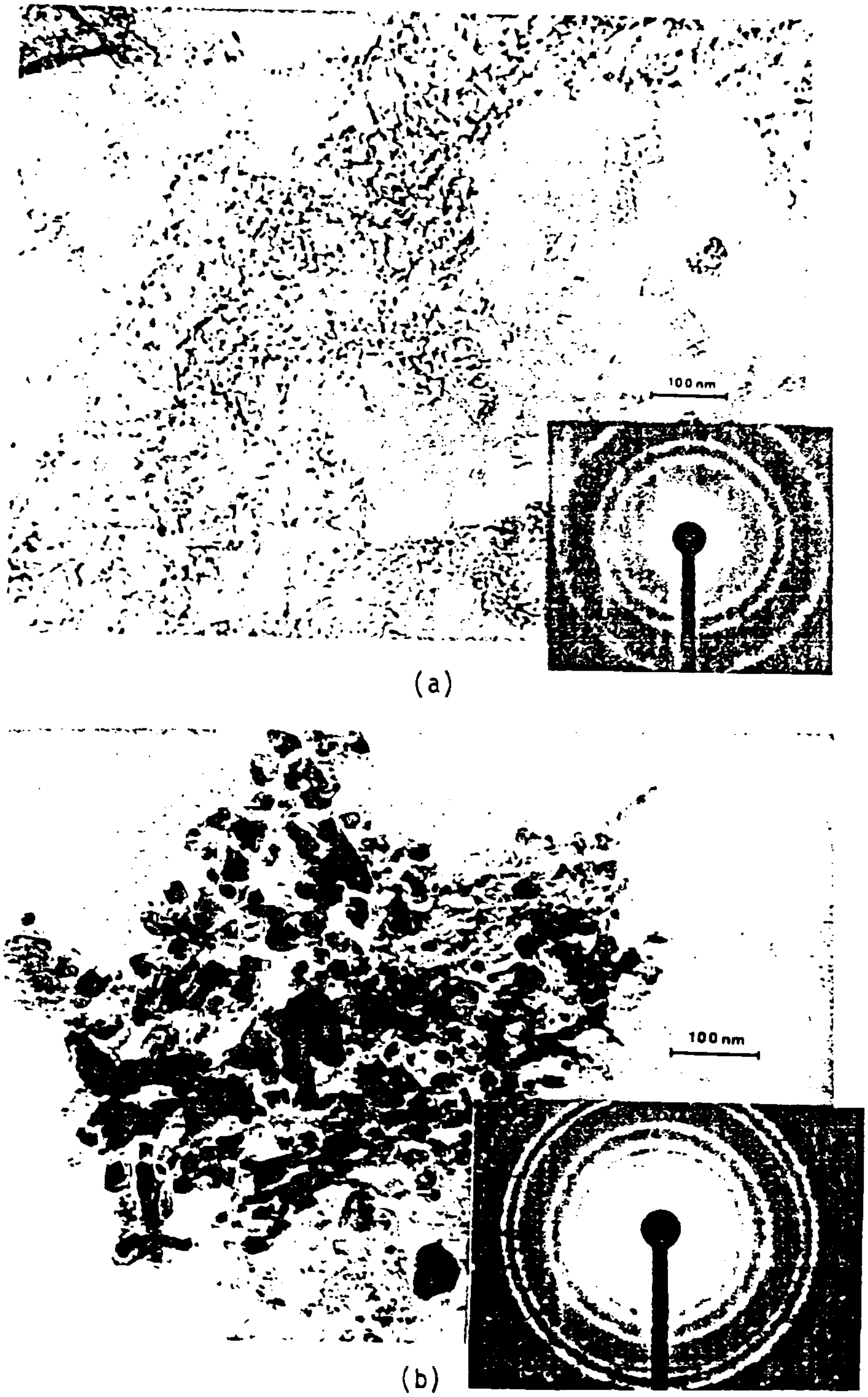

Figure 4. Transmission Electron Micrographs of Dispersed Spinel Powder, Calcined at (a) 550°C and (b) 1000°C in Air for One Hour.

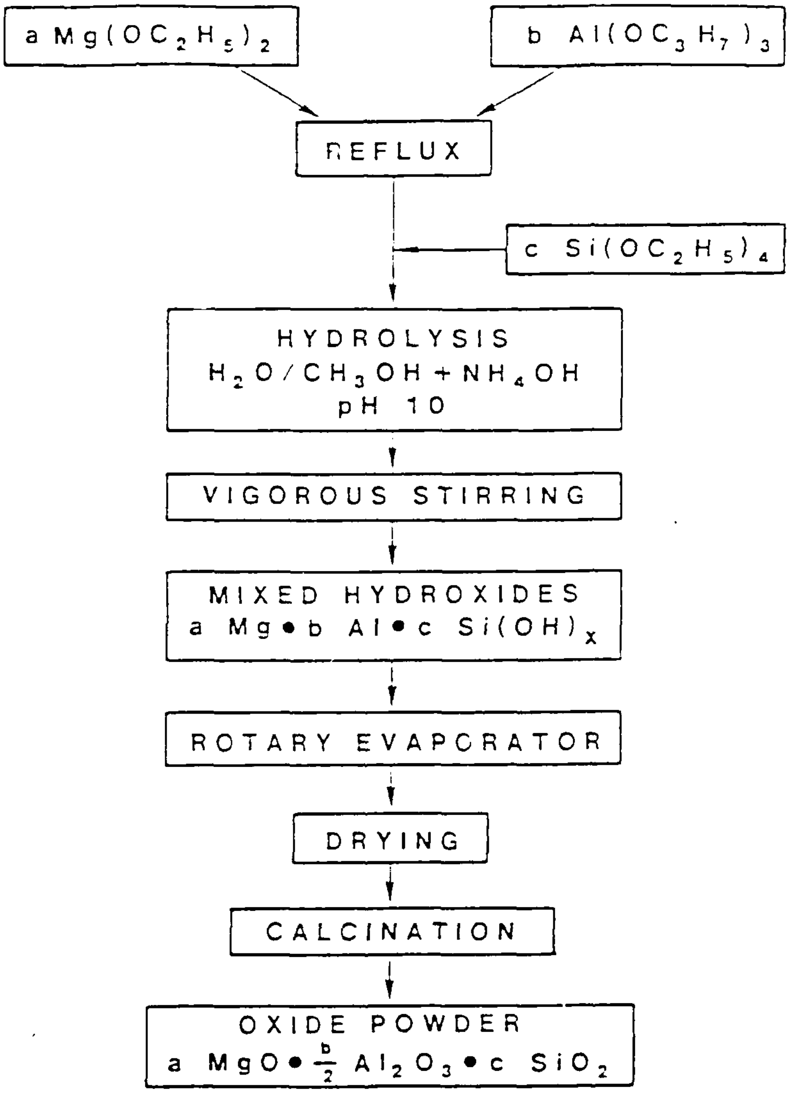

Figure 5. MAS (Cordierite) Powder Preparation from Mixed Metal Alkoxides.

SILICON OXYNITRIDE AND Si-Al-O-N CERAMICS FROM ORGANOSILICON POLYMERS

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INTRODUCTION

Preceramic polymers whose pyrolysis provides silicon containing ceramics such as silicon carbide, silicon nitride, silicon oxynitride, and sialon have received great research interests.[1] These preceramic polymers provide a unique approach for the process of ceramic shape forming.[2] At relatively low temperatures, these preceramic polymers can be converted into coatings, fibers, powders, and monoliths with the desired physical properties and chemical compositions.

The objective of our current research is to develop new types of organosilicon polymers which can be converted into useful ceramic materials such as silicon oxynitride and sialon. In this chapter we are reporting the synthesis of new organosilicon polymers and their application in thin film coating and ceramic-ceramic composite fabrication.

Preparation of Organosilicon Polymers and its Conversion to Ceramics

Seyferth, et al.,[3] have developed a process for the preparation of useful preceramic polymers by using CH_3SiHCl_2 as the starting material. The ammonolysis of CH_3SiHCl_2 in THF produced an oligomer $[CH_3SiHNH]_n$ ($\bar{n} \sim 5$).

Dehydrocyclodimerization of this low molecular weight cyclic oligomer with a base catalyst such as KH, form a reactive polysilylamide, $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHK)_c]_n$. This reactive polysilylamide can react with various Si-H bonds containing organosilicon polymers to produce new hybrid polymers.

One example of this application is in the preparation of Si_2ON_2 precursor polymers by reacting $[CH_3SiHNH]_n$ with cyclic $[CH_3Si(H)O]_m$ (hydrolysis product of CH_3SiHCl_2 in CH_2Cl_2) in the presence of catalytic amounts of KH. Detailed descriptions of the polymer synthesis were previously reported.[1c] In one approach ("In-Situ" Method) the hybrid polymer was prepared by mixing (∿ 1:1 by weight) of $[CH_3SiHNH]_n$ and $[CH_3Si(H)O]_n$ in the THF solution and then added to a suspension of a catalytic amount of KH in THF. After quenching with an electrophile, such as CH_3I, the white hybrid polymer was obtained in good yield (∿ 90%). This hybrid polymer is very soluble in organic solvents (hexane, toluene, THF) and was used for the following coating experiments and ceramic-ceramic composite fabrications.

Okamura, et al.,[4,5] have shown that Si_2ON_2 fibers can be obtained by pyrolyzed polycarbosilane fibers (cured precursor fiber of NICALON) under flowing NH_3 gas. Similarly, pyrolysis of hybrid polymers under a stream of NH_3 gas also produces white Si_2ON_2 powder.[1c] It is suggested that the high temperature nucleophilic cleavage of the Si-CH_3 bonds by NH_3 occurred with the loss of CH_4 gas. Pyrolysis of the hybrid polymer to 1000°C, under inert atmosphere, generating a black ceramics in 84% yield (by TGA). More significantly, we have found that pyrolysis of the hybrid polymer, under flowing NH_3 gas to 800°C, provided Si_2ON_2 powder in 86% yield which when analyzed by elemental analysis, contained only 0.15% carbon. X-ray powder diffraction (XRD) patterns of the ceramic sample hot-pressed at 1700°C exhibited only Si_2ON_2. A transmission electron microscopic (TEM) study was also performed to analyze the microstructure of the above mentioned sample. TEM samples were made by mechanically thinning, followed by ion milling.

FIG-1

The bright-field micrograph, shown in Fig. 1, represents the typical microstructure of Si_2ON_2. Grains of polyhedral shape were present. Frequent overlapping of grains were observed throughout the electron transparent region of the samples. Due to grain overlapping, Morie fringes were also found. The average grain size was found to be ∿ 1960 Å. Figure 1 also includes the transmission electron diffraction (TED) pattern. The presence of diffraction spots are indicative of the crystalline nature of the sample. Although the diffraction spots (in the TED pattern) are present from the various grains, the symmetrical spot pattern can be indexed in terms of an orthorhombic structure with [200] orientation. The lattice parameters of this structure are found to be close to that reported in ASTM (#18-1171). This TED result is consistent with XRD analysis described earlier. The presence of diffuse streaks connecting the diffraction spots are indicative of the stacking disorder (planar faults) present in the individual grains.

Conventional methods for the preparation of Si_2ON_2[6] involve the high temperature nitridation reaction of a mixture of silicon and silicon dioxide with metal oxide as catalysts. In addition to the formation of Si_2ON_2, the product always contains Si_3N_4 and unreacted SiO_2. Pyrolysis of hybrid polymers under flowing NH_3 gas provides an alternative method for the preparation of pure Si_2ON_2 ceramic material in good yield.

Thin Film Coating

One of the potential applications of preceramic polymers is the formation of a thin film coating of the ceramic material.[7] The refractory character and chemical stability of Si_2ON_2 make it an attractive candidate as an oxidatation resistant coating for materials,[8] such as carbon-carbon composites. Hybrid polymers derived Si_2ON_2 also provide a low temperature processing and fabrication method for electronic application, specifically, as a dielectric layer for microelectronic circuitry.[9] It has been shown that nitridation of the sol-gel derived silicon dioxide film can convert this film partially to silicon oxynitride film.[9] However, these films were shown to be highly non-homogeneous, with a predominance of nitrogen at the surface.[10] The Si_2ON_2 precursor polymer can be easily dissolved in organic solvents producing a solution with different vicosity, which is ideal for cast film. No curing is needed since the polymer is self-curing. Therefore, the application of hybrid polymers can provide an inexpensive method for the desirable dense, uniform, well-bonded, Si_2ON_2 coating.

The Si_2ON_2 thin films were prepared by the following method. The polysiloxane-polysilazane hybrid polymer was dissolved in toluene. The polymer solution was deposited on a single crystal n-type <111> silicon wafer using a spin-coating technique. The wafer was placed on a spin coater and cleaned with acetone and methanol just before use. The polymer solution was then dropped onto the wafer and the wafer was spun at 1000-4000 rpm for 30 seconds. The polymer film was air dried overnight. Thermal treatment of the polymer film was carried out under a stream of flowing NH_3 gas to 800°C, heated at 100°C/hr.

The thickness of the polymer coatings obtained by this process depends upon the solution concentration and the spinning speed. Concentrations in the ranges of 2.5-20% were found to produce coherent polymer and ceramic coatings with good adherence to the wafers. The polymer film thickness prepared by the 2.5% solution (4000 rpm) was on the order of 500 Å and the thickness of the ceramic film after subsequent heat treatment was on the order of 300 Å. Coated surfaces were examined by SEM to determine their overall homogeneity. In general, Si_2ON_2 films are observed to be smooth and adhere well to the surface of the substrate. No porosity can be found on the film. However, when 30% concentration polymer solution was used, a thick coating with mud like cracks were obtained after thermal treatment. More experiments are needed to prepare thick, monolithic, and crack-free ceramic films.

CERAMIC-CERAMIC COMPOSITES

The ceramic-ceramic composites with glass or glass-ceramics as matrices have limits on shapes and sizes, on the other hand, polymer infiltration and pyrolysis into the ceramic matrix can be a potential processing route for complex shaped composites.[11] The candidate ceramic precursor polymers should possess the following properties: 1) processable, i.e, meltable or soluble in a solvent, 2) air stability, 2) high ceramic-conversion yield, 4) resulting ceramic should be refractory, and 5) relatively low pyrolysis temperature. The Si_2ON_2 precursor hybrid polymer is a good matrix candidate material for ceramic-ceramic composite. Although the bulk density of the composite may be low and the volume shrinkage severe, the low processing temperature (< 800°C) and low weight loss (85% yield) make the hybrid polymer very attractive.

Various ceramic fibers were first incorporated with the hybrid polymer and composite pyrolysis followed. The purpose of this preliminary research is to study the compatibility of polymer derived Si_2ON_2 matrix and ceramic fiber. NICALON and CELION (carbon fiber) fibers in both continuous and chopped forms were used for this experiment. The ceramic fibers were first soaked in a concentrated hybrid polymer solutions of hexane, then the resulting green body was dried in air. Pyrolysis of the green body was performed under a stream of flowing NH_3 gas to 800°C with a heating rate of 100°C/hr. The surface scanning electron micrographs (SEM) of the Si_2ON_2/NICALON unidirectional composites are shown in Fig. 2. The microstructure exhibits substantial transverse cracking between fibers. Other than these cracks, the matrix appears to be very dense. The bonding between matrix and fibers appears to be moderate. The almost regular cracking exhibited by the composite is caused by gas evolution and volume shrinkage of polymer during pyrolysis. The SEM micrographs of the fracture surface of the Si_2ON_2 chopped carbon fiber composite are shown in Fig. 3. This composite exhibited areas of high Si_2ON_2 content and obvious transverse cracks between fibers. After thermal treatment under flowing NH_3 gas, the carbon fibers did not appear to degrade. The bonding between matrix and carbon fiber appears to be weaker than that of the NICALON fiber; Fig. 3 clearly shows an impression of the carbon fiber on the matrix.

Si-Al-O-N Systems

Hydrolytic decomposition of metal alkoxides have attracted great research interest. However, the potential of using metal alkoxides in conjunction with organosilicon polymers to prepare processable multicomponent preceramic polymers has not been fully explored.[12] Okamura[5] reported that by mixing polycarbosilane, the precursor polymer of NICALON, with titanium tetrabutoxide and heated at ∿ 200°C, a polytitanocarbosilane polymer was synthesized. The reaction is proposed to have occurred at the Si-H bond of polycarbosilane and formed a Si-O-Ti bond. Therefore, it is possible that the reaction of Si-H containing hybrid polymers with various metal alkoxides will also form the expected Si-O-M (M = Al, Ti, or Zr) linkage in the new organometallic silicon polymers.

Our first approach to the Si-Al-O-N system involved physically blending hybrid polymer (Si_2ON_2 precursor) with $Al(OC_3H_7)_3$ (Al_2O_3 precursor) in a 1:1 weight ratio. The blended polymer was then pyrolyzed under flowing NH_3 gas to 800°C. No reaction occurred between silicon hybrid polymer and $Al(OC_3H_7)_3$ and only white Si_2ON_2 powder was obtained after pyrolysis. In another approach, the hybrid polymer was physically blended with aluminum hydoxides [hydrolysis product of $Al(OC_3H_7)_3$] and then pyrolyzed under a stream of NH_3 gas to 800°C, producing a gray ceramic powder. The ceramic yield was excellent (> 85%). The gray powder was subjected to further heat treatments under argon, up to 1620°C, with only minimal weight loss. Chemical composition of the ceramic material by elemental analysis revealed the presence of silicon, aluminum, oxygen, and nitrogen elements.* X-ray powder diffraction of the ceramic material exhibits diffraction patterns of mullite ($3Al_2O_3 \cdot 2SiO_2$) and trace amounts of α-Al_2O_3. Based on the chemical analysis and XRD data, the nitrogen (6.5 wt.%) containing phase remains in an amorphous form.

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* Insufficient oxidation of the sample prevent elucidation of exact chemical composition.

CONCLUSION

Potentially, silicon oxynitride can be just as good a ceramic as silicon nitride. The material is stable up to 1550°C in an inert atmosphere and has an oxidation resistance superior to that of silicon nitride in the range of 1400 to 1750°C when exposed to air. The major advantage of Si_2ON_2 prepared from hybrid polymer over the conventional methods is that stoichiometric Si_2ON_2 can be obtained at low temperatures with high purity and the absence of minor phases. The hybrid polymer can be prepared by readily available, and relatively cheap, polysiloxane and polysilazane and its composition can be easily modified by varying the mixing ratio of these two precursor oligomers. The polymers are white solids with excellent characteristics for ceramic coatings having no heavy metal contamination. Smooth and well adhered Si_2ON_2 coating on silicon wafer can be achieved by low temperature ($< 800C$) heat treatment of the hybrid polymer film. High ceramic conversion yield made these polymer ideal for ceramic-ceramic composite fabrication. From this preliminary study, it was found that Si_2ON_2 and carbon fibers are potentially good combinations for ceramic-ceramic composites. The absence of strong bonding between carbon fibers and Si_2ON_2 matrix should provide greater toughness for these composites. Through the reaction of hybrid polymers with aluminum hydroxides, polymer precursor systems can be extended from the Si_2ON_2 to the Si-Al-O-N system.

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REFERENCES

1. Representative of recent publications:

   a. D. Seyferth and Y. F. Yu, U.S. Patent 4639,501, Jan 27, 1987.

   b. G. E. Lagrow, T. F. Lim, and J. Lipowitz, J. Am. Ceram. Soc. Bull. 66, 363-367 (1987)

   c. Y. F. Yu and T-I. Mah, "Better Ceramics Through Chemistry II," Mater. Res. Soc. Symp. Proc., Vol. 73, C. J. Brinker, D. E. Clark, and D. R. Ulrich, eds. (1986), pp. 559-563.

   d. C. L. Schilling, J. P. Wesson, and T. C. Williams, Am. Ceram. Soc. Bull. 62, 912 (1983).

   e. R. West, J. Maxka, R. Sinclair, P. M. Cotts, Polymer Preprints, 28, 387 (1987).

   f. K. Okamura and Y. Hasegawa, J. Mater. Sci. 21, 321-328 (1986).

2. R. W. Rice, Bull. J. Am. Ceram. Soc. 62, 889 (1983).

3. D. Seyferth, G. H. Wiseman, C. A. Poutasse, J. M. Schwark, and Y. F. Yu, Polymer Preprints, 28, 389 (1987).

4. K. Okamura, M. Sato, Y. Hasegawa, and T. Amano, Chem. Lett. 2059 (1984).

5. K. Okamura, M. Sato, and Y. Hasegawa, Proceedings of the Fifth International Conference on Composite Materials, San Diego, CA, 1985, pp. 535-542.

6. a. M. E. Washburn, Bull. J. Am. Ceram. Soc. 46, 667 (1967).

   b. M. E. Washburn, U.S. Patent No. 3,356,513 (Dec. 5, 1968).

   c. M. E. Washburn, U.S. Patent No. 3,639,101 (Feb. 1, 1972).

7. L. V. Interrante, L. E. Carpenter,II, C. Whitmarsh, and W. Lee, Better Ceramics through Chemistry II, Mater. Res. Soc. Symp. Proc. Vol. 73, C. J. Brinker, D. E. Clark, and D. R. Ulrich, eds., (1986) pp. 359-366.

8. R. K. Brow and C. G. Pantano, Appl. Phys. Lett. 48, 217 (1986).

9. L. A. Carman and C. G. Pantano, Chapter 20, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., Wiley, NY, 1986, pp. 187-200.

10. R. K. Brow and C. G. Pantano, Better Ceramics through Chemistry, Mater. Res. Soc. Symp. Proc., Vol. 32, C. J. Brinker, D. E. Clark, and D. R. Ulrich, eds., (1984) pp. 361-367.

11. K. S. Mazdiyasni, R. West, and L. D. David, J. Am. Ceram. Soc. 61, 504 (1978).

12. A. G. Williams and L. V. Interrante, Better Ceramics through Chemistry, Mater. Res. Soc. Symp. Proc., Vol. 32, C. J. Brinker, D. E. Clark, and D. R. Ulrich, eds., pp. 151-156, 1984.

Figure 1

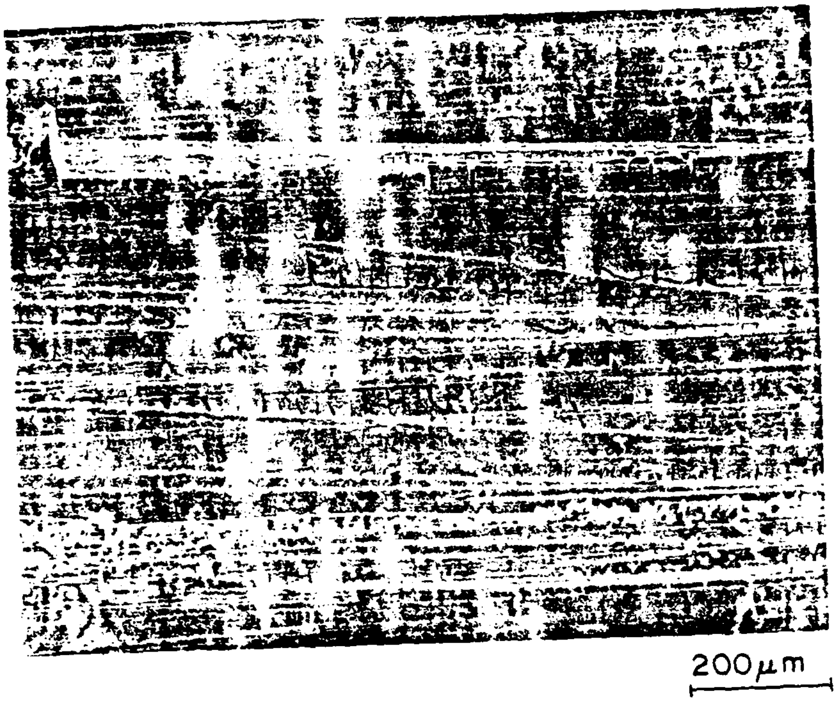

Figure 2

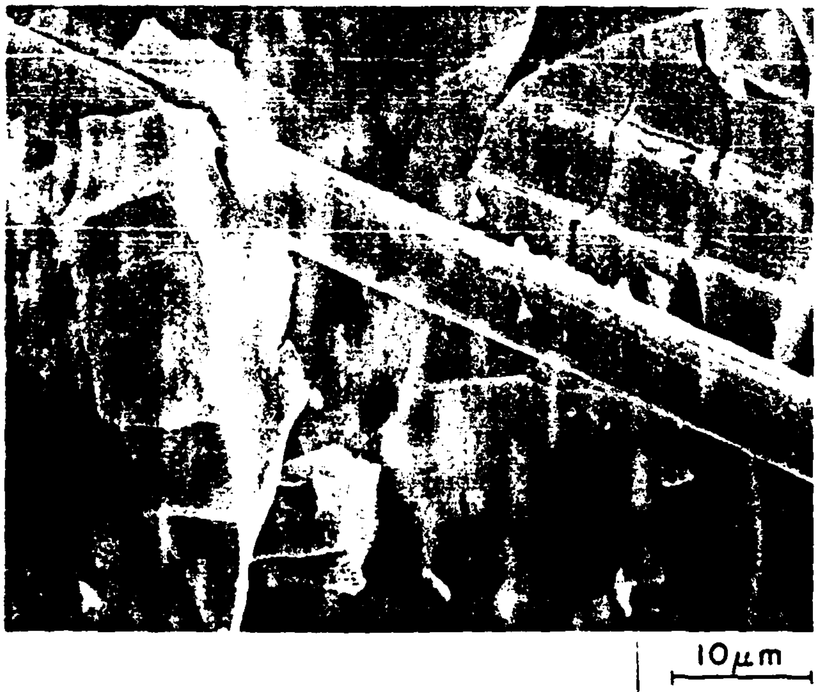

Figure 3

Chapter LEGENDS

Yu and Mah

Silicon Oxynitride and Si-Al-O-N Ceramics from Organosilicon Polymers

Fig. 1. TEM Micrograph of Hybrid Polymer Derived Si_2ON_2 Ceramics (Hot-Pressed at 1700°C).

Fig. 2. SEM Micrograph of Si_2ON_2/NICALON Continuous Fiber Composite.

Fig. 3. SEM Micrograph of Si_2ON_2 Chopped Carbon Fiber Composite.

SOL-GEL PROCESSING OF TRANSPARENT $MgAl_2O_4$

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ABSTRACT

High-purity, transparent monolithic spinel ($MgAl_2O_4$) was synthesized via the hydrolytic thermal decomposition of mixed alkoxide organo-metallic precursors. Several factors, such as the metal alkoxide concentration in various solvents, the water to solvent ratio and the reaction temperatures affect the hydrolysis of the mixed alkoxides. These factors also influence the transparency of the resulting sols and gels. The degree of transparency of the sols and gels is also influenced by such factors as pH and drying control chemical additives. Variations in the processing conditions during drying, aging, and sintering of the gels produced ceramic materials with a high degree of transparency.

INTRODUCTION

Spinel ($MgAl_2O_4$) has good chemical stability, low thermal expansion, and good elevated temperature strength and toughness. $MgAl_2O_4$ is generally prepared by the fusion of the component oxides. The main drawback, using the conventional method of spinel preparation, is the lack of an economical fabrication process to produce material having an optical grade at a reasonable cost [1,2]. The objective of this work is to demonstrate the formation of transparent $MgAl_2O_4$ materials through sol-gel methods.

EXPERIMENTAL

Mixed Metal Alkoxide Preparation

The mixed alkoxide $MgAl_2(OR)_8$ can be prepared by combining the single alkoxides, $Mg(OC_2H_5)_2$ and $Al(O^iC_3H_7)_3$. These reactions are summarized in the following equations.

$$Mg(s) + C_2H_5OH \xrightarrow{HgI_2} Mg(OC_2H_5)_2$$

$$Al(s) + CH_3C_2H_5OH \xrightarrow{HgCl_2} Al(O^iC_3H_7)_3$$

$$Mg(OC_2H_5)_2 + 2Al(O^iC_3H_7)_3 \xrightarrow[\Delta]{} MgAl_2(OC_2H_5)_2(O^iC_3H_7)_6$$

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Transparent Gel Preparation

A flow diagram of the the steps involved in preparing the gel-derived transparent spinel is shown in Fig. 1.

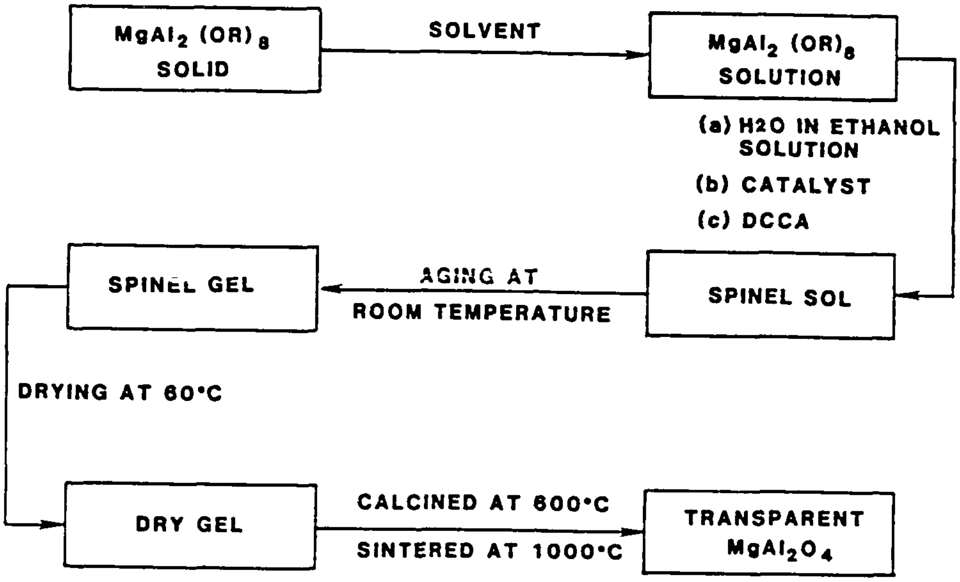

Figure 1. Flow Diagram of Transparent $MgAl_2O_4$ Preparation.

Magnesium-aluminum double alkoxide solid [$MgAl_2(OR)_8$] was mixed with various quantities of 100% pure ethanol (C_2H_5OH) and stirred thoroughly to form a clear solution. Distilled water was added to the pure ethanol to prepare water/ethanol solutions in different concentrations. These water/ethanol solutions were then added slowly to the alkoxide/ethanol solution while being vigorously stirred. The additions are accomplished at two different temperatures--room temperature and 60°C.

We have studied the effect of three acids (HCl, CH_3COOH, and HNO_3) on the hydrolysis and sol-gel formation. Each acid was slowly added to the solution by two different methods. It was added to the water/ethanol solution to prepare an acidified water/ethanol solution, or added directly into the double alkoxide solution. Differing amounts of the acids were also used. Foramide ($HCONH_2$), acetamine (CH_3CONH_2), triethanolamine $(OHC_2H_4)_3N$, and oxalic acid (HO_2CCO_2H) were used as drying control chemical additives (DCCA), and were added directly into the double alkoxide solution, while the total volume of DCCA/ethanol remained unchanged.

Only those conditions, which resulted in a clear sol, were selected for subsequent aging and drying experiments. After one day, gelation usually had started in the transparent clear sol. The clear gels, for various periods of time, were allowed to age at room temperature. These gels were then dried at 60°C in an oven for one week. Calcination and densification of these transparent gels were accomplished by first heating at 600°C, and then, slowly raising the temperature to 1000°C.

RESULTS AND DISCUSSION

In our research efforts to prepare a transparent $MgAl_2O_4$ ceramic, there were three major goals: 1) to prepare a clear transparent sol which can be converted into a clear transparent gel, 2) to convert the transparent gel, at higher temperature, to a polycrystalline spinel ceramic, while retaining its transparency, and 3) to prepare large transparent spinel ceramics with no cracks and good strength.

The amount of water and its concentration in the ethanol solution can determine the degree of hydrolysis and type of initial product formed, thus, influencing the secondary polymerization reactions [3]. The resultant polymer molecules will, therefore, be affected both chemically and structurally. We have investigated the effect of water to double metal alkoxide in the gelation process. The molar ratio of alkoxide to H_2O ranged from 10:1 to 1:1. The water/alkoxide ratios between 2.5 and 4 produced the best transparent gels. The effects of hydrolysis temperature in the spinel sol-gel process appear to be less significant that the temperature effects observed in the hydrolysis of $Si(OC_2H_5)$. The gels derived from the 60°C hydrolyzed sols formed slightly larger pieces of uncracked ceramic materials than the room temperature hydrolyzed sols. When larger amounts of ethanol were used to dissolve the double alkoxide, larger pieces of the gel resulted after aging and drying. These gels also remained transparent after 600 and 1000°C heat treatment. The powder XRD pattern of the spinel gels at 600°C show only background diffraction, while the samples heated to 1000°C showed broad peaks of $MgAl_2O_4$ spinel.

It has been well documented that the catalyst used in a gelation reaction can have large effects on the microstructure of the gels formed, as well as the kinetics of the gelation process. The additions of acids, such as HCl, CH_3COOH, and HNO_3, in our attempts to prepare transparent gels produced only cloudy solutions. The mole ratio of alkoxide/acid used is in the range of 0.1 to 0.01. Additions of excess acid, to clear up the solution only prevented it from gelling over a one-week period. Drying control chemical additives(DCCA) [4], such as $HCONH_2$, CH_3CONH_2, and oxalic acid have been utilized to improve the transparency of the resultant sols. The gels processed using the DCCA are optically transparent and retain their shape with no crack formation after low temperature drying. However, with subsequent heating above the DCCA boiling point, clear gels foamed.

The effect of $Si(OC_2O_5)_4$ addition on the gelation, as well as drying, was also studied. Small amounts of $Si(OC_2H_5)_4$ were first hydrolyzed in the presence of an acid catalyst and then added to the double alkoxide solution. The resulting gels showed good resistance to cracking during the aging and drying processes. However, the addition of TEOS reduced the degree of transparency of the resulting ceramic materials.

CONCLUSION

Results of this study demonstrate the potential for forming transparent spinel ceramic materials, using the sol-gel processing techniques. Further work is needed to understand the conversion of sols and gels to ceramics and to reduce the severe cracking which develops during the drying process.

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REFERENCES

1. A. Gatti, R.L. Mehan, and M.J. Noone, "Development of a Process for Producing Transparent Spinel Bodies," General Electric, Final Report under Contract N00019-71-0126.

2. K. Jones, T.J. Davis, H.G. Emblem, and P. Parkes, in Better Ceramics through Chemistry, II, edited by C.J. Brinker, E.E. Clark, and D.R. Ulrich, (Mater. Res. Soc. Symp. Proc. 73, Palo Alto, CA 1986) p. 111.

3. J.D. Mackinzie, "Applications of the Sol-Gel Method: Some Aspects of Initial Processing," in Science of Ceramic Chemical Processing, edited by L.L. Hench and D.R. Ulrich, Wiley, NY, 1986, Chapter 12.

4. L.L. Hench, "Use of Drying Control Chemical Additives in Controlling Sol-Gel Processing," in Science of Ceramic Chemical Processing, edited by L.L. Hench and D.R. Ulrich, Wiley, NY, 1986, Chapter 4.

FINAL REPORT

(SEPT. 87 TO MAR. 88)

SOL-GEL SYNTHESIS OF HIGH Tc SUPERCONDUCTORS

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MSE 492
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Abstract:

The sol-gel synthesis technique was used to prepare homogeneous starting powders as the precursors to the superconducting materials ($YBa_2Cu_3O_{7-x}$). The research emphasized using alkoxide derived yttrium, barium, and copper as the starting components. Two ways of mixing the starting materials together were explored during the course of this research. The results obtained from this research will be discussed. Physical and chemical properties of the two mixing methods will be compared as well as effect of calcination and sintering temperatures on the susperconducting samples.

Introduction:

In the past decade, the highest critical superconducting temperature (T_c) able to be achieved was 23 K, obtained using a Nb_3Ge alloy[1]. In late 1986, the discovery of superconductivity at 36 K in a La-Sr-Cu-O system, by Bednorz and Muller[2], stimulated wide research effort in the field of superconductivity Through this effort, several research teams increased the T_c of the La-Sr-Cu-O system to 40 K.(3-5) The T_c was then pushed above the liquid nitrogen temperature (77 k) by Wu[6], using a multiphase Y-Ba-Cu-O system. Chu's group, at the University of Houston, announced in Feb. 87 that they had observed the transition onset temperature as high as 92 K. During this exciting time, the physics of these materials received more attention than their chemistry.

Most reports on the preparation of superconducting materials indicated that only solid state reactions between Y_2O_3, CuO, and $BaCO_3$ were being used. Some of the problems associated with the powders produced from solid state reactions are: inhomogeneity, non-uniformity (in terms of particle size and shape), and high-impurity levels of the powders. Although the materials fabricated from these powders exhibited superconducting behavior, the densities of the samples were low, which lead to non-reversibility in the electrical responses during warming back to room temperature.[7] Another problem associated with solid state reactions are that the decomposition temperature of $BaCO_3$ is high, requiring high sintering temperatures to convert the carbonate to oxide. These sintering temperatures exceed the orthorhombic to tetragonal phase transformation temperature (occurring at ~700 °C). It was discovered that the orthorhombic phase is responsible for high temperature superconductivity in the Y-Ba-Cu-O system[8] and as a result of the phase transformation at high sintering temperature, oxygen leaves the orthorhombic structure and, therefore, the superconductive phase is partially lost.

One way to avoid using $BaCO_3$ as a starting component is to use barium alkoxide as the source of barium. The sol-gel technique provides this possibility. In the last few years, the sol-gel methods have been receiving a great deal of scientific attention among ceramic and glass scientists. The word "sol", according to Jirgensons and Straumanis, describes the dispersion of colloids in liquids. Colloids are in turn described as solid particles with diameters in the range of 10 - 1000 Å, each containing 10^3 - 10^9 atoms. When the viscosity of a sol increases sufficiently, usually through evaporating of solvents, it becomes rigid. This rigid material is termed a "gel". Some advantages of the sol-gel methods over the conventional method include better homogeneity from raw materials, better purity, and lower processing temperatures.

The objective of this project was to prepare homogeneous precursor materials at low temperatures, and converting these precursors into superconducting powders by the use of the sol-gel method.

Experimental Procedure:

This research emphasized the use of metal alkoxides for the preparation of high-purity oxide precursors. The three metal alkoxides were $Y(OR)_3$, $Ba(OR)_2$, and Cu(OR)2, where R represents an organic group.

The synthesis of the three metal alkoxides is summarized by the following reactions:

(1) $$Y^\circ + 3C_3H_7OH \xrightarrow{HgCl_2} Y(OC_3H_7)_3 + 3/2H_2$$

(2) $$Ba^\circ + 2C_2H_5OH \xrightarrow{60^\circ C} Ba(OC_2H_5)_2 + H_2$$

(3) $$CuCl_2 + 2Na(OC_2H_5OH)_2 \xrightarrow{24^\circ C} 2NaCl + Cu(OC_2H_5)_2$$

The preparation of precursor powders was approached by two different conditions of hydrolysis.

The first condition was to decompose each metal alkoxide individually with an excessive amount of degassed CO_2 free water solution to form a hydroxide gel. Each hydroxide gel was dried and calcined at different temperatures (600°C, 700°C, 850°C, 950°C) for converting into oxide powders. The proper amounts of each alkoxide derived powder was mixed together to produce mixture of $YBa_2Cu_3O_{7-x}$. A pellet was pressed from each mixture after calcining at different temperatures and then sintered at a corresponding calcination temperature under a flowing stream of oxygen for 12 hours.

The second condition involved mixing the three components together in an alkoxide form and then proceeding with the hydrolysis. However, according to Eq.(3), a trace amount of NaCl was formed during the synthesis of copper alkoxide. This NaCl could not be removed from the alkoxide powder, and therefore, produced impurities in the mixture. In addition to that, copper alkoxide was found not to be completely soluble in the mixture. As a result, copper(II) acetate was substituted for copper alkoxide because copper(II) acetate has a better solubility in ethanol. The hydroxide slurry of the three components was obtained after the hydrolysis process. The slurry was vacuum dried and calcined at various temperatures to remove all residual carbon groups and water. After the calcination process, an oxide mixture of $YBa_2Cu_3O_{7-x}$ was obtained. A pellet was pressed from the calcined powders and sintered at the same temperature as the calcination temperature under flowing of oxygen.

Samples prepared from the two conditions of hydrolysis and calcined at various temperatures were analysized by x-ray diffraction in order to characterize the superconductive phase ($YBa_2Cu_3O_{7-x}$) as a function of sintering temperatures. The particle size of the powders was determined from an alcohol dispersion of the powders sprayed onto a carbon coated grit and viewed via the transmission electron microscope.

The densities of the samples were determined by measuring the diameters and the thicknesses of the specimens and were substituted in the following equation.

$$\text{Density} = \frac{\text{mass}}{\pi\left(\frac{d^2}{4}\right)t}$$

where d is the diameter and t is the thickness.

The microstructure of the samples were examined by using high power microscope.

Results and Discussion:

In the first condition, the calcination processes of yttrium and copper hydroxides were done successfully without an intermediate reaction between the powders and the crucibles. The infrared spectra of yttrium oxide and copper oxide in the 200 to 4000 cm^{-1} region were obtained for investigation of the results of the synthesis to check the completeness of reaction and for product identification. The characteristic peaks were found for both oxide powders. However, during the calcination process of $Ba(OH)_2$, the hydroxide powder started to melt and react with the alumina crucible at ~ 450°C. This probably was due to the decomposition of barium hydroxide monohydrate ($Ba(OH)_2$ H_2O) that had formed during the calcination process. The infrared spectrum of BaO calcined at 400°C showed strong $BaCO_3$ characteristic peaks. The formation of $BaCO_3$ was thought to be a reaction between BaO and CO_2 caused by air which somehow got into the system.

X-ray diffraction patterns of the powders calcined at the various temperatures showed only individual component characteristic peaks, instead of the complex "123" phase.

The second condition showed promising results. X-ray diffraction patterns showed that the superconductive "123" phases started to appear at calcination/sintering temperatures higher than 850°C. Calcination/sintering temperatures below 850°C, again, showed only the individual component characteristic peaks. The average particle size was found to be 0.04 to 0.05 μm (by STEM photomicrograph analysis). However, larger individual particles were found. These averaged in size from 0.1 to 0.2 μm. Energy dispersion x-ray analysis (EDX) of the powders showed a 1:2:3 composition (YBaCu). The densities of the samples sintered below 850 °C were calculated to be only 65% of theoretical density, while the densities of those sintered at temperatures higher than 850°C were measured to be ~85% of theoretical density. The microstructure of the sol-gel derived samples which were sintered at 950°C, indicated a much finer grain size compared to the grain size of the samples produced from conventional methods. The average width of the grains ranged from 2 to 3 μm and the average length of the grains ranged from 10 to 20 μm. The grains were found to contain some twinning deformations as a result of the tetragonal to orthorhombic phase transformation. Samples sintered at temperatures below 950°C exhibited relatively poor to no Meissner effects.

Conclusion:

Powders produced from the sol-gel method were shown to be extremely fine. The mixing condition where the three components were mixed together in the alkoxide form and then hydrolyzed produced "123" powders. Ultra-fine powders lead to better densification of the sintered samples (~85% of T.D). Finer grain sizes were observed in the microstructures of the sintered samples produced by the sol-gel method. The study of the superconductive phase, as a function of calcination/sintering temperatures has indicated that the complex "123" phase appears at temperatures higher than the $BaCO_3$ decomposition temperature (~850°C).

References

1. L. R. Testardi, R. L. Meek, J. M. Poate, W. A. Royer, A. R. Storm, and J. H. Wernick, Phys. Rev., B11, 4304 (1975).

2. J. B. Bednorz and K. A. Muller, Z. Phys., B64, 189 (1986).

3. K. Kishio, K. Kitazawa, S. Kanbe, I. Yasuda, N. Sugil, H. Takgi, S. Uchida, K Fueki, and S. Tanaka, Chem. Lett., (Japan) 492 (1987).

4. J. G. Bednorz and K. A. Muller, Z. Phys., B64, 189 (1986).

5. J. M. Tarascon, L. H. Greene, W. R. Mckinnon, G. W. Hull, and T. H. Beballe, Science, 238, 1373 (1987).

6. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. O. Wang, and C. W. Chu, Phys. Rev. Lett., 58, 908 (1987).

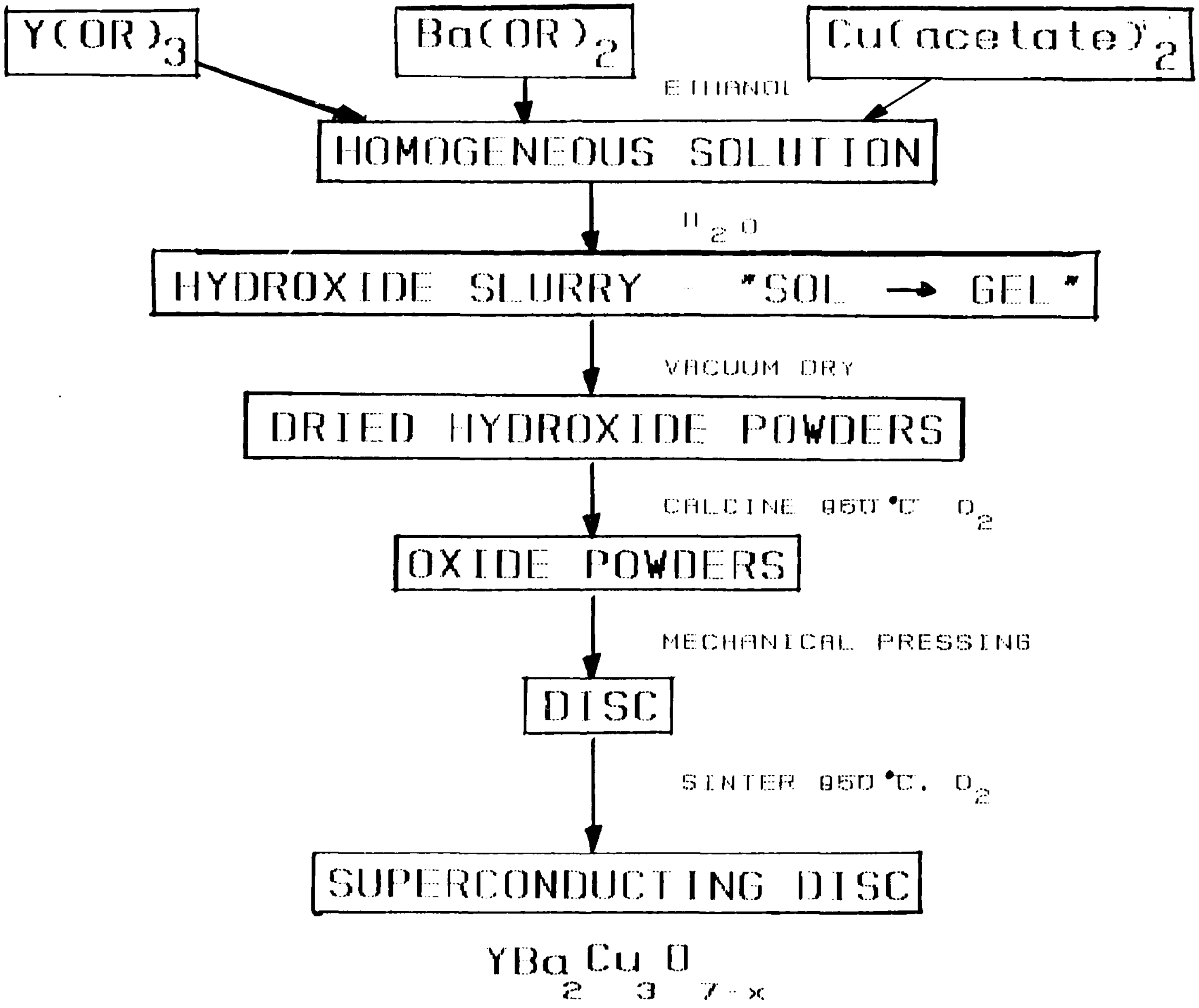
7. M. J. Cima and W. E. Rhine, "Powder Processing for Microstructural Control in Ceramic Superconductors," Advanced Ceramic Materials, Vol. 2, No. 3B, 329 (1987).

8. D. J. Eaglesham, C. J. Humphreys, W. J. Clegg, M. A. Harmer, N. Alford, and J. D. Birchall, "The Othorhombic and Tetragonal Phases of $Y_1Ba_2Cu_3O_{9-y}$," Advanced Ceramic Materials, Vol. 2, No. 3B, 662 (1987).

9. J. M. Tarascon, P. Barboux, B. G. Bagley, L. H. Green, W. R. Mckinnon, and G. W. Hull, "High - Temperature Superconducting Oxide Synthesis and the Chemical Doping of Cu-O planes," American Chemical Society, 1987, Chapter 20.

10. K. S. Mazdiyasni, "Powder Synthesis from Metal - Organic Precursors," Ceram. Inter., 8 42 (1982).

SCHEMATIC OF SOL-GEL PROCESS



$Y(OR)_3$

$Ba(OR)_2$

$Cu(acetate)_2$

ETHANOL

HOMOGENEOUS SOLUTION

H_2O

HYDROXIDE SLURRY "SOL → GEL"

VACUUM DRY

DRIED HYDROXIDE POWDERS

CALCINE 850 °C O_2

OXIDE POWDERS

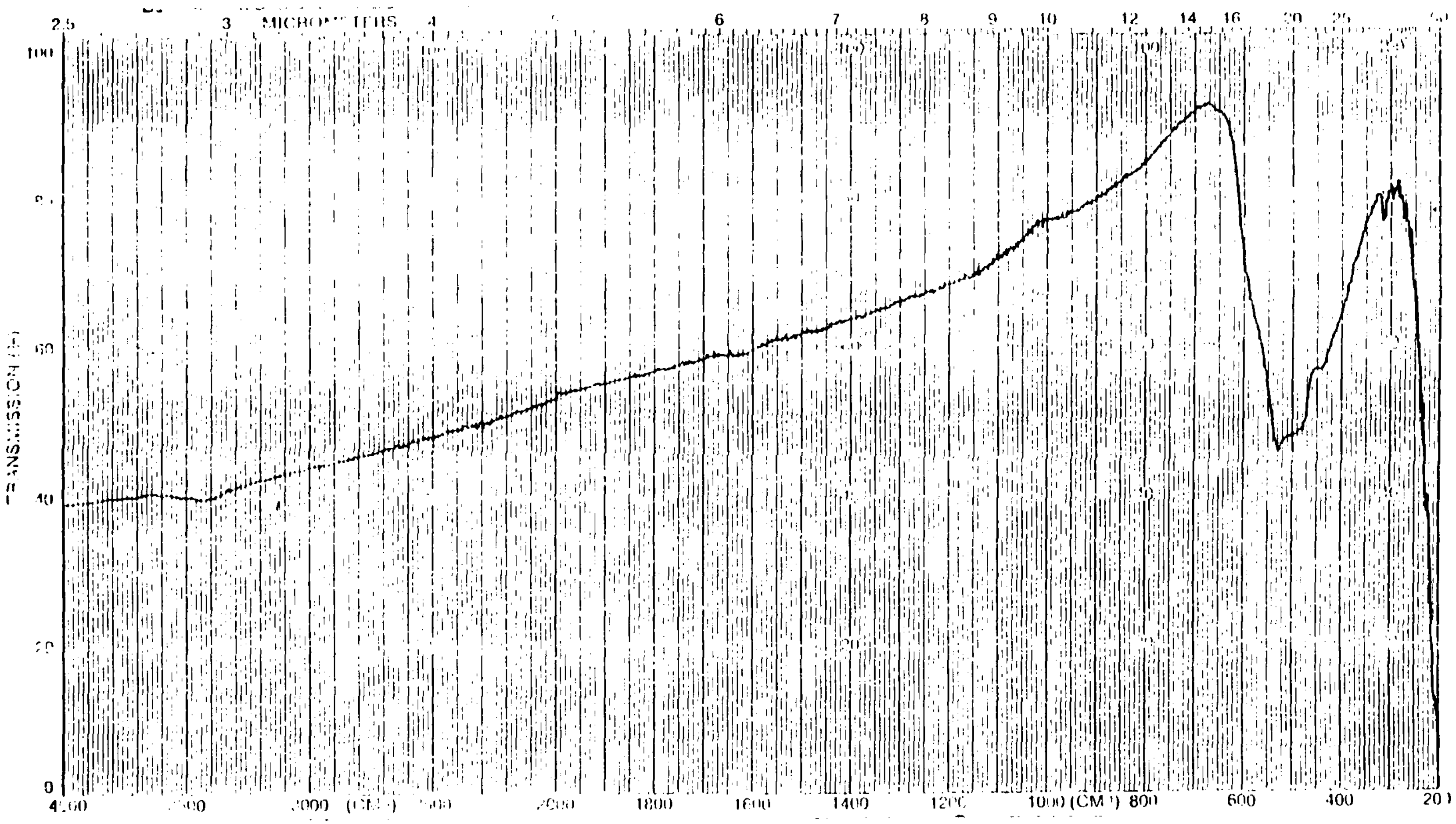
MECHANICAL PRESSING

DISC

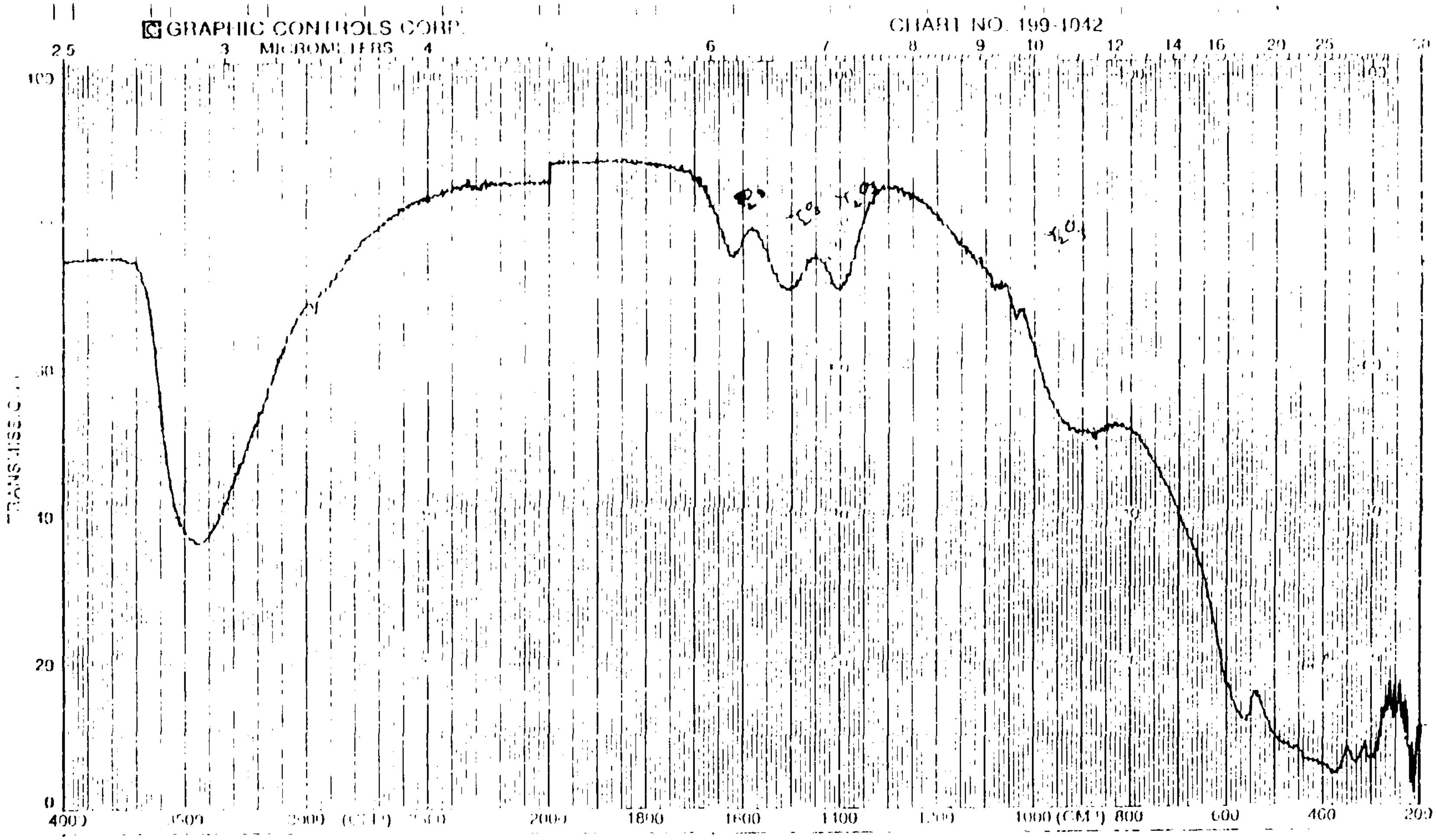
SINTER 850 °C. O_2

SUPERCONDUCTING DISC

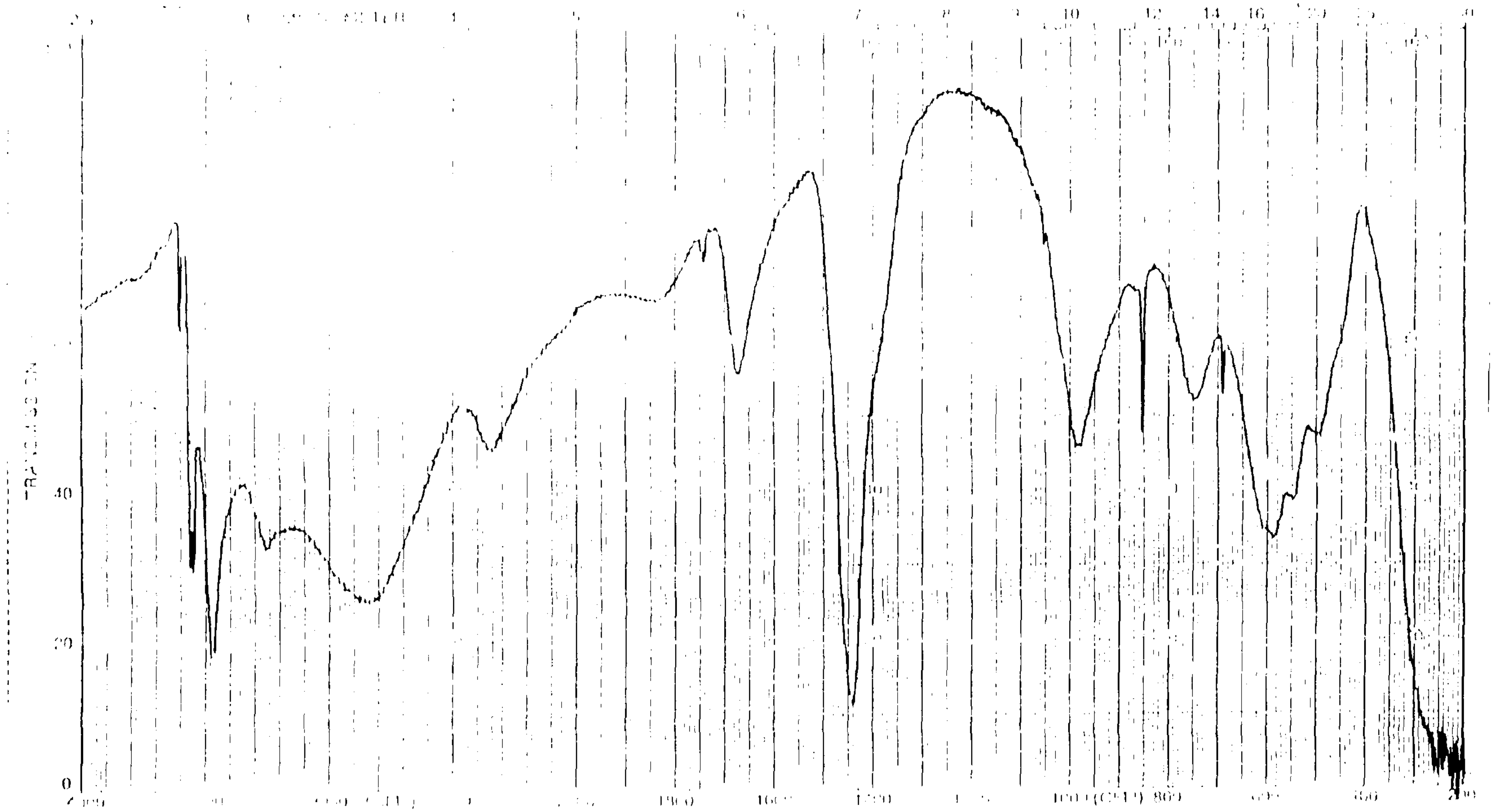
$YBa_2Cu_3O_{7-x}$



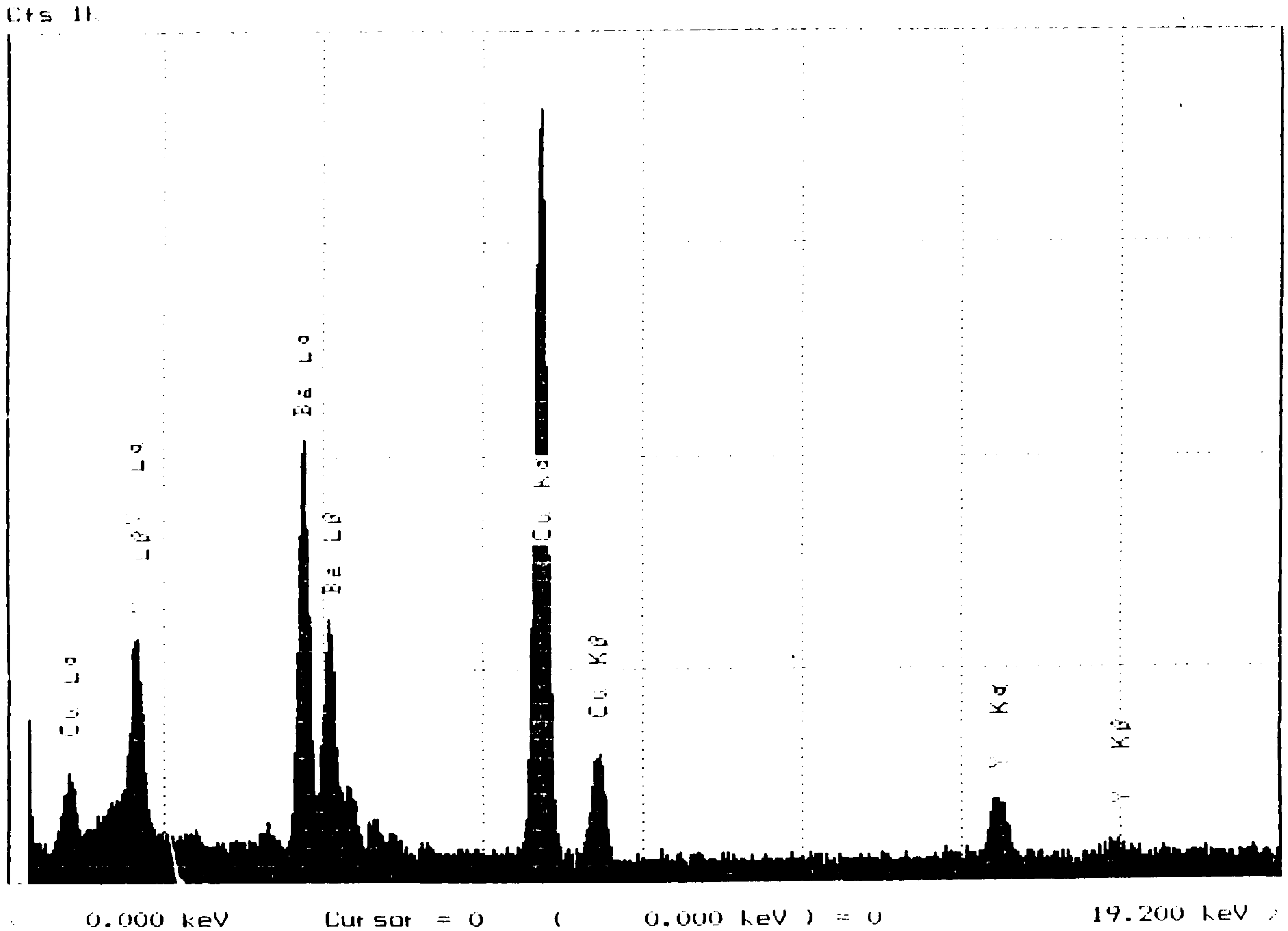
Infrared Spectrum of CuO



Infrared Spectrum of Y_2O_3



Infrared Spectrum of BaO shows $BaCO_3$ peaks

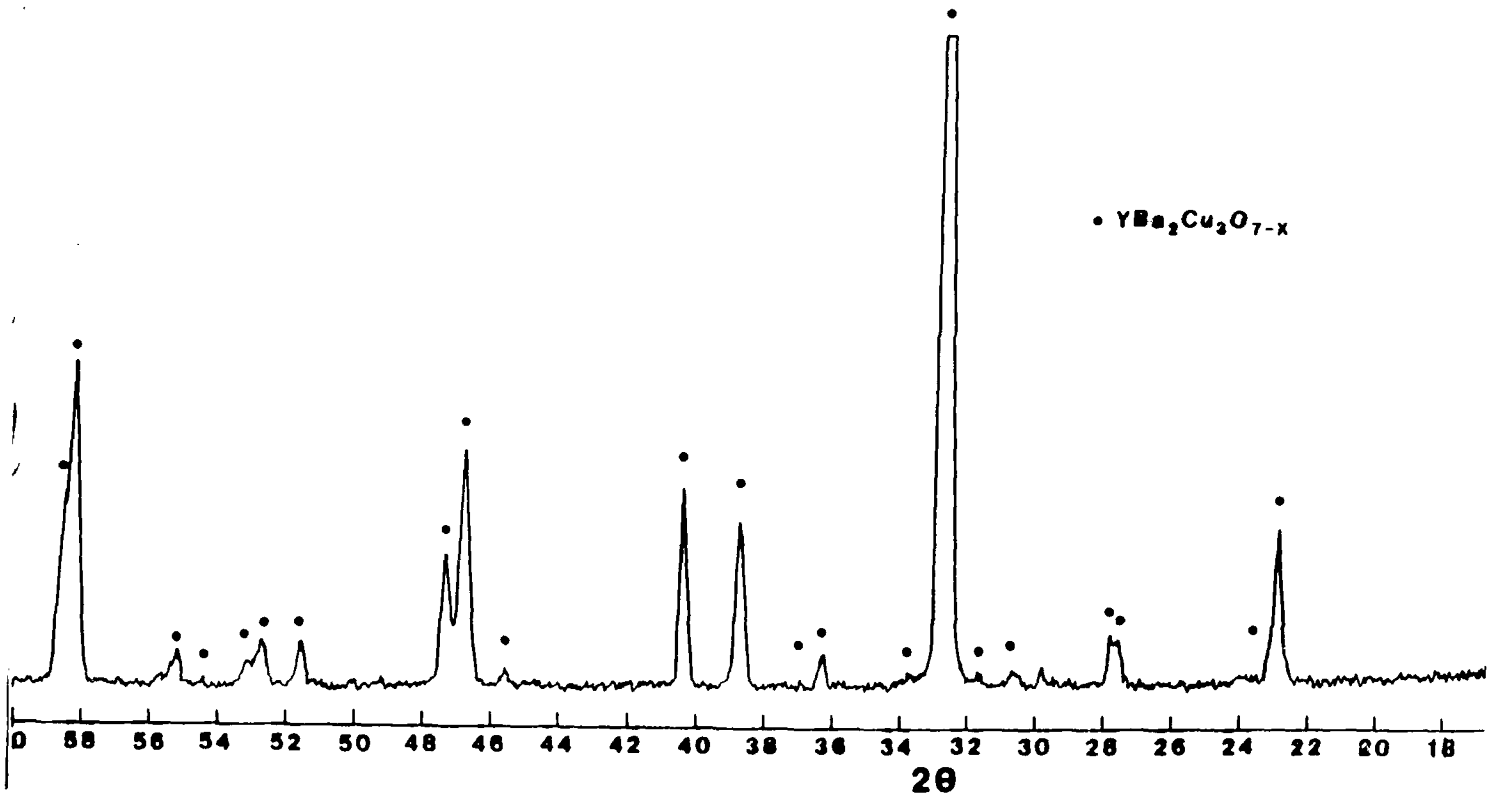


Energy Dispersion X-ray Analysis

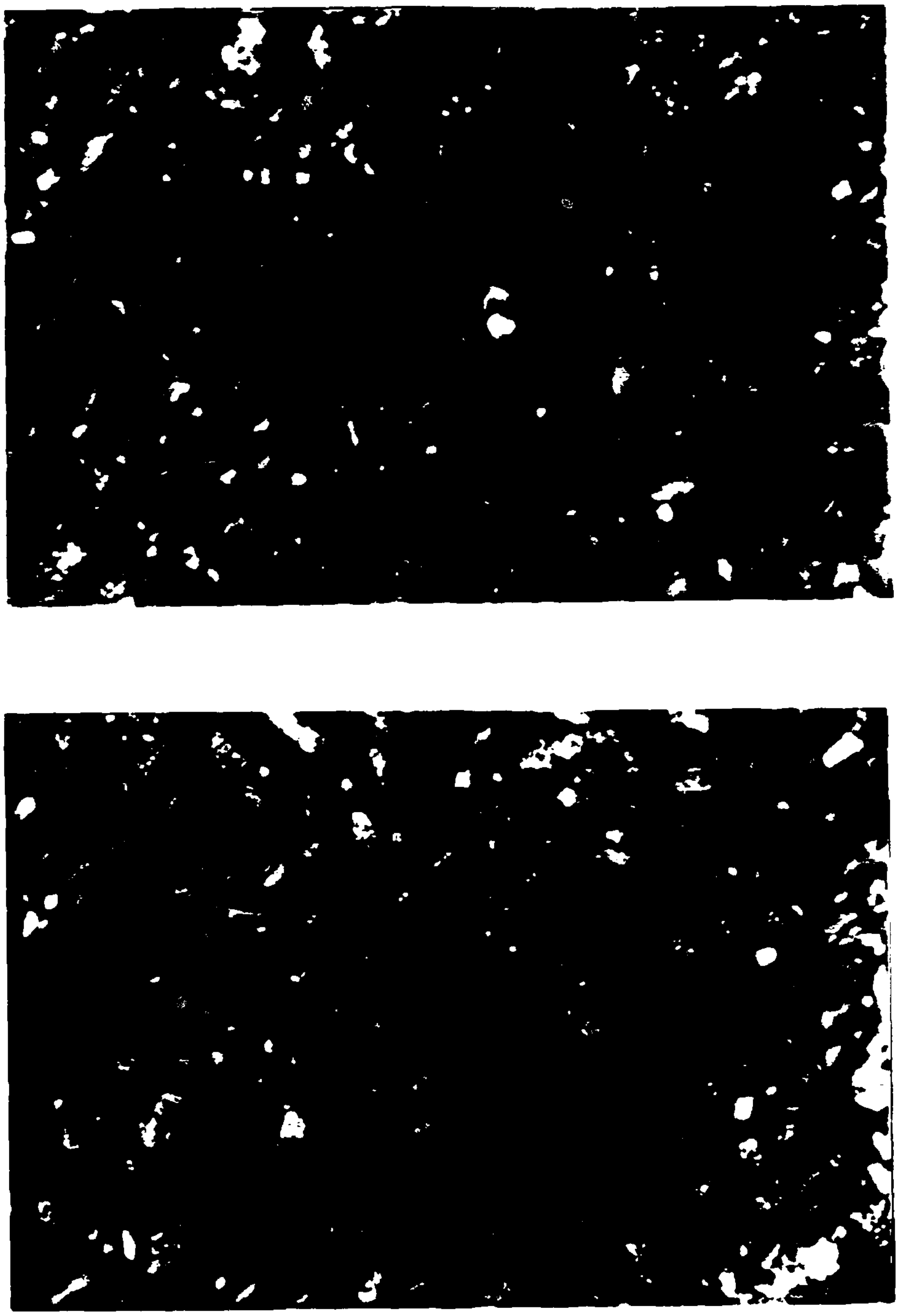
of the powders shows '123' composition

TEM MICROGRAPH OF Y $Ba_2Cu_3O_{7-x}$ POWDER AFTER 950°C CALCINATION FOR 12 HOURS UNDER FLOW OF O_2

TEM MICROGRAPH OF ISOLATED $YBa_2 Cu_3 O_{7-X}$ PARTICLES GROWN DURING 950°C CALCINATION FOR 12 HOURS UNDER FLOW OF O_2



X-ray diffraction of '123' phase
of superconductor



Microstructure of superconductor $YBa_2Cu_3O_{7-x}$

derived from sol-gel method