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ULTRASTRUCTURE PROCESSING AND ENVIRONMENTAL STABILITY OF ADVANCED STRUCTURAL AND ELECTRONIC MATERIALS

FINAL REPORT

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Submitted by

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The objective of our Multi-Investigator Research Program is to achieve an understanding of the science of chemically derived, ultrastructure processing of ceramics, glasses and composites. Five research areas were pursued.

(A) Sol-Gel Processing: Procedures for reliable and reproducible drying of sol-gel silica monoliths were developed using drying control chemical additives (DCCA's). Processes for chemical stabilization of ultraporous, optically transparent silica monoliths were also developed along with the means for chemically doping of optically active polymers. A method for dehydration and densification of the ultrapure silica monoliths was also achieved resulting in optical components with uniquely low optical transmission from 160 nm to 3500 nm. the gel-derived optical silica also has a uniquely low coefficient of thermal expansion over a broad temperature range. The processing and properties of GELSIL™ made by this new ultrastructure processing method are reviewed in:

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19. ABSTRACT (Continued)

(B) Sol-Gel Derived Processing of Ceramic Coatings and Composites: Electrophoretic and thermophoretic methods for depositing composite coatings onto a carbon/carbon substrate have been developed. A gradient coating has been achieved where a concentration of SiC whiskers is varied throughout the thickness.

(C) Organometallic Precursor Processing of SiC Composites: A method for efficient chemical crosslinking of polysilanes has been developed and utilized in producing a range of composites containing SiC. After pyrolysis superior toughness to weight ratios are obtained for these ultrastructural composites to the nm scale of SiC reinforcement.

(D) Electronic Characterization of High Band Gap Silicon Carbide: Significant advances have been made in measuring and interpreting the noise spectrum and transport properties of SiC single crystals. This work has led for the first time to verification of the general theory of space charged limited flow (SCL) of semiconductors developed by Prof. Van Vliet several years ago.

(E) General Research on Inorganic Materials: A quantitative theory of technology transfer has been developed using examples from the MIRP. Other investigations on glass surface chemistry and environmental resistance have also been pursued.

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COMPLETED PROJECT SUMMARY

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objective of our Multi-Investigator Research Program is to achieve an understanding of the science of chemically derived, ultrastructure processing of ceramics, glasses and composites. Five research areas were pursued.

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"Ceramics and the Challenge of Change", L. L. Hench, Advanced Ceramic Materials 3[3] (1988) 203-206.

LIST OF PUBLICATIONS

"Use of Drying Control Chemical Additives (DCCAs) in Producing Gel Monoliths," L. L. Hench in Glass...Current Issues, A. F. Wright and J. Dupuy, eds., Martinus Nijhoff Publishers, Dordrecht, The Netherlands, 1985, pp. 259-262.

"NMR Raman Study of the Effect of Additives on the Sol-Gel Process," I. Artaki, M. Bradley, T. W. Zerda, J. Jonas, G. Orcel and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 73-80.

"Comparative Pore Distribution Analysis of Sol-Gel Derived Silica," S. Wallace and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 148-156.

"Physical Properties of Partially Densified SiO_2 Gels," S. Park and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 168-172.

"Sol-Gel Derived Silica Optical Filters," S. H. Wang and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 201-207.

"Processing and Structural Properties of Li_2O-Al_2O_3-TiO_2-SiO_2 Gels," G. Orcel and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 224-230.

"Physical-Chemical and Biochemical Factors in Silica Sol-Gels," L. L. Hench and G. Orcel, J. Non-Crystalline Solids 82 (1986) 1-10.

"Processing and Structural Evolution of (xLi_2O $(1-x)Na_2O$) Al_2O_3 $2SiO_2$ Gels," G. Orcel, J. Phalippou, and L. L. Hench, J. Non-Crystalline Solids 82 (1986) 301-306.

"Structural Changes of Silica Xerogels During Low Temperature Dehydration," G. Orcel, J. Phalippou and L. L. Hench, J. Non-Crystalline Solids 88 (1986) 114-130.

"Effect of Formamide Additive on the Chemistry of Silica Sol-Gels, Part I: NMR of Silica Hydrolysis," G. Orcel and L. L. Hench, J. Non-Crystalline Solids 79 (1986) 177-194.

"Sol-Gel Glass," L. L. Hench, McGraw Hill Yearbook of Science and Technology, 1987, pp. 221-223.

"Polarized Infrared Reflection Spectroscopy of Single Crystal Lithia-Silicates and Quartz," W. J. McCracken, W. B. Person, and L. L. Hench, J. of Materials Science 20 (1985) 3853-3864.

"Sol-Gel Derived Ceramic Matrix Composites," D. E. Clark, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley & Sons. 1986, 237-246.

"Processing of Sol-Gel Derived Doped Powders and Substrates," K. W. Wistrom and D. E. Clark, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley & Sons. 1986, 272-277.

"Thermophoretic and Electrophoretic Deposition of Sol-Gel Composite Coatings," W. J. Dalzell and D. E. Clark, Ceramic Engineering and Science Proceedings, 7[7-8], (1986) 1014-1026.

"Use of FT-IRRS for Characterizing Thermal Stability of SiC Whiskers and Composites," G. P. LaTorre, R. A. Stokell, R. H. Krabill and D. E. Clark, Ceramic Engineering and Science Proceedings, 7[7-8], (1986) 933-944.

"Effect of Surface Hydration on Polymer Adsorption," Brij M. Moudgil and Yeu-Chyi Cheng, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley & Sons. 1986, 550-554.

"Electrophoretic Behavior and Surface Reactions of Sol-Gel Derived Alumina," B. I. Lee and L. L. Hench, Colloids and Surfaces 23 (1987) 211-229.

"Crosslinking and Pyrolysis of Silane Precursors for Silicon Carbide," B. I. Lee and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 345-353.

"Silicon Carbide/Silica Gel Matrix Composites," B. I. Lee and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 231-236.

"Silicon Carbide/Silica Molecular Composites," B. I. Lee and L. L. Hench in Ceramic Engineering and Sciences Proceedings, Am. Ceram. Soc., Columbus, Ohio, July-August 1986, pp. 994-997.

"Observation of Single Carrier Space-Charge Limited Flow in Nitrogen-Doped α-Silicon Carbide. I. I-V Characteristics and Impedance," S. Tehrani, J. S. Kim, L. L. Hench, C. M. Van Vliet and G. Bosman, J. Appl. Phys. 58[4] (1985) 1562-1570.

"Observation of Single Carrier Space-Charge Limited Flow in Nitrogen-Doped α-Silicon Carbide. II. I-V Electrical Noise," S. Tehrani, L. L. Hench, C. M. Van Vliet and G. Bosman, J. Appl. Phys. 58[4] (1985) 1572-1577.

"The Role of Chemical Additives in Sol-Gel Processing," L. L. Hench, G. Orcel and J. L. **Nogues** in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 35-47.

"SAXS Study of Silica Sols and Gels," G. Orcel, R. W. Gould and L. L. Hench in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 289-294.

"Processing and Properties of $x\text{SiO}_2\text{-}(1\text{-}x)\text{Al}_2\text{O}_3$ Gels," G. Orcel, J. Phalippou, and L. L. Hench, Rev. Int. Hautes Temper. Refract. Fe. 22 (1985) 185-190.

"Optical Properties of Gel-Silica Glasses," Shi-Ho Wang, Candace Campbell and L. L. Hench to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Dielectric Relaxation Analysis of Gel Drying, S. Wallace and L. L. Hench to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Sol-Gel Coatings on Carbon/Carbon Composites," S. M. Sim, R. H. Krabill, W. J. Dalzell, Jr., P-Y. Chu, and D. E. Clarkin Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 647-652.

"Drying Behavior of Sol-Gel Derived Al_2O_3 and Al_2O_3-SiC Composites," R. H. Krabill and D. E. Clark in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 641-646.

"Chemically Derived Refractory Coatings," S. M. Sim. P-Y. Chu, R. H. Krabill and D. E. Clark, to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Surface Charge of Sol-Gel Derived Aluminas as a Function of Calcination Temperature," Burtrand I. Lee and Larry L. Hench, Particulate Science and Technology 4 (1986) 213-223.

"Silicon Carbide from Organosilanes and Application in Silica Gel Glass Composites," B. I. Lee and L. L. Hench in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 815-822.

"Observation of Single Carrier Space-Charge-Limited Flow in Nitrogen Doped α-Silicon Carbide. III. Computer Calculations," S. Tehrani, G. Bosman, L. L. Hench and C. M. Van Vliet, J. Appl. Physics 60[7] (1986) 2386-2395.

"New Perspectives of Silicon Carbide: An Overview, With Special Emphasis on Noise and Space-Charge-Limited Flow," Carolyn M. Van Vliet, Gijs Bosman, and Larry L. Hench, Ann. Rev. Mater. Sci. 18 (1988) 381-421.

"Gel-Silica Optics," L. L. Hench, S. H. Wang, and J. L. Nogues, in Multifunctional Materials, Vol. 878, Robert L. Gunshor, ed., SPIE, Bellingham, WA, 1988, pp. 76-85.

"Correlations Between Processing Parameters, Ultrastructure, and Strength of Gel-Silica," J. K. West, R. Nikles, and G. LaTorre, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Physical Properties of Dried Na_2O-SiO_2 Monoliths," R. Li and L. L. Hench, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Physical and Structural Evolution of Sol-Gel Derived TiO_2-SiO_2 Glasses," Y. C. Cheng and L. L. Hench, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Dielectric Relaxation Analysis of Water Adsorption in Sol-Gel Derived Silica Gel Monoliths, S. Wallace and L. L. Hench to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Preparation and Characterization of Monolithic Si-Ce-O Gels," A. Sivade, G. Orcel, L. L. Hench, J. Bouaziz, R. Sempere, D. Bourret, presented at the 40th Pacific Coast Regional Meeting of the American Ceramic Society, San Diego, CA, Nov. 3, 1986.

"Gel-Silica Waveguides," R. V. Ramaswamy, T. Chia, R. Srivastava, A. Miliou and J. West, in Multifunctional Materials, Vol. 878, Robert L. Gunshor, ed., SPIE, Bellingham, WA, 1988, pp. 86-93.

"Coating Porous Substrates by the Sol-Gel Method," P-Y. Chu and D. E. Clark, presented at the 89th Annual Meeting and Exposition of the American Ceramic Society, Pittsburgh, PA, April 27, 1987.

"Molecular Composites of SiC/SiO_2, SiC/Al_2O_3, and SiC/TiC," Burtrand I. Lee and Larry L. Hench, Am. Ceram. Soc. Bull. 66[10] (1987) 1432-1485.

"Comparison of Polysilastyrene with Polycarbosilane as a Precursor to Silicon Carbide," B. I. Lee, presented at the Fiber Tex-87, Nov. 3-5, 1987, in press.

"Mechanical Properties of Partially Densified SiC/SiO_2 Gel Matrix Composites," B. I. Lee and L. L. Hench, in Ceramic Engineering and Science Proceedings, Am. Ceram. Soc., Westerville, Ohio, 8[7-8], 1987, 685.

"Theory and Experiments of 1/f Noise in Schottky-Barrier Diodes Operating in the Thermionic-Emission Mode," Min-Yih Luo, Gijs Bosman, Aldert van der Ziel, and Larry L. Hench, IEEE Transactions of Electron Devices 35[8] (1988) 1351-1356.

"Ceramics and the Challenge of Change," L. L. Hench, Advanced Ceramic Materials 3[3] (1988) 203-206.

"Corrosion of Silicate Glasses: An Overview," L. L. Hench, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

OVERVIEW

The goal of our Multi-Investigator Research Program (MIRP) is to achieve an understanding of the science of ultrastructure processing of ceramics, glasses and composites. Ultrastructure processing as used in our program and in this report refers to the manipulation and control of chemistry based processes for the purpose of attaining a new generation of high performance materials with predictable properties and insensitivity or control of harsh environments for use in space, structural, optical, electronic, electro-optical or heat engine applications.

We are pursuing three parallel chemistry based approaches to produce ultrastructure processed materials. Primary emphasis (75% effort) of the MIRP is devoted to the science and application of sol-gel processing. The rationale for this heavy emphasis on sol-gel processing is the low thermal requirements to produce materials in this way and the unique physical properties that result.

An important material characteristic of sol-gel derived materials is the very large (30-50%) percentage of microporosity in the materials after drying. Consequently a wide range of physical properties can be achieved with materials of the same chemical composition by varying the volume fraction, size distribution, and connectivity of the microporosity. Microporosity gradients are possible and impregnation of microporous structures to produce a wide range of composite materials is also possible. Preparation of sol-gel derived materials with reinforcing whiskers, fibers, or weaves is also possible resulting in an even wider range of properties.

Consequently, one of our operating hypotheses for the MIRP is that understanding the chemistry of sol-gel derived materials will make it possible to achieve unique combinations of physical properties to fulfill a broad range of design objectives.

Because of the scale of this objective we are pursuing two parallel paths in our sol-gel studies.

Project A is focused on the chemistry of sol-gel derived silica and silicate systems. Figure 1A illustrates the ultrastructural changes during drying and densification of a sol-gel derived material. Figure 1B is the actual processing temperature-time scale utilized to produce ultrapure sol-gel derived silica (GELSIL™) optical components.

During this contract we have made considerable progress in learning how to produce monolithic dried gel structures rapidly and reliably. Drying control chemical additives (DCCA's) were used to control the drying stresses. Several manuscripts have been published (see Publication List) describing our studies of the DCCA system and ultrastructural characterization of sol-gel processing of silica and silicate monoliths. Twelve patents have been applied for protecting the DCCA concept and its optimization. Optical doping of SiO_2 with transition metals and rare-earth oxides have been developed and patent applications have been filed.

A broad range of important new physical properties of SiO_2 monoliths has been achieved by controlling every step of the sol-gel process. An especially important finding is that sol-gel derived ultrapure silica (GELSIL™) has a lower optical absorption, and lower coefficient of thermal expansion than melt derived or fume processed vitreous silicas.

The data on GELSIL™ indicates that it may be the first truly intrinsic photonic conductor in the UV-vis-NIR range. GELSIL™ also has an uniquely low thermal expansion coefficient over a broad temperature range.

Figure 1A

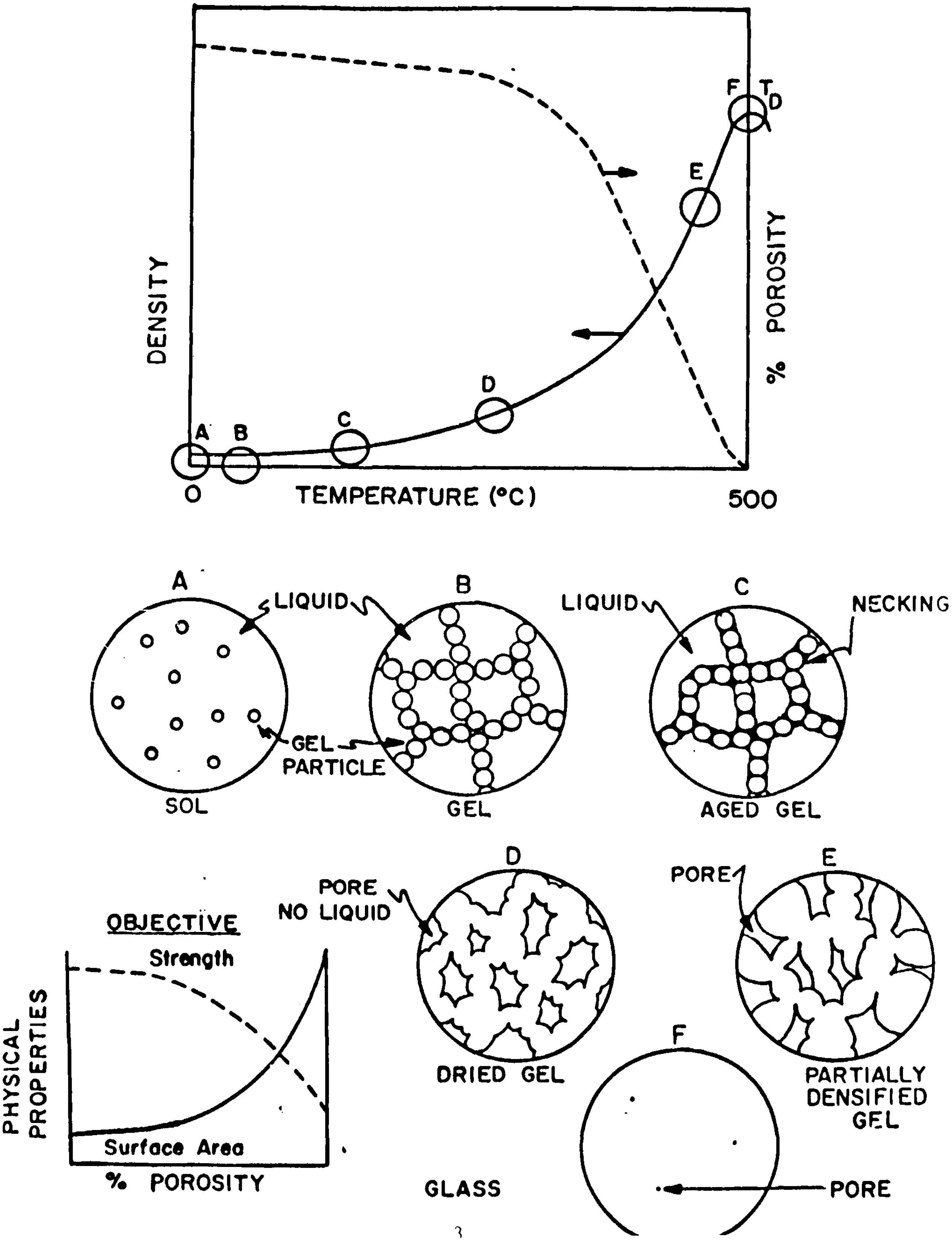
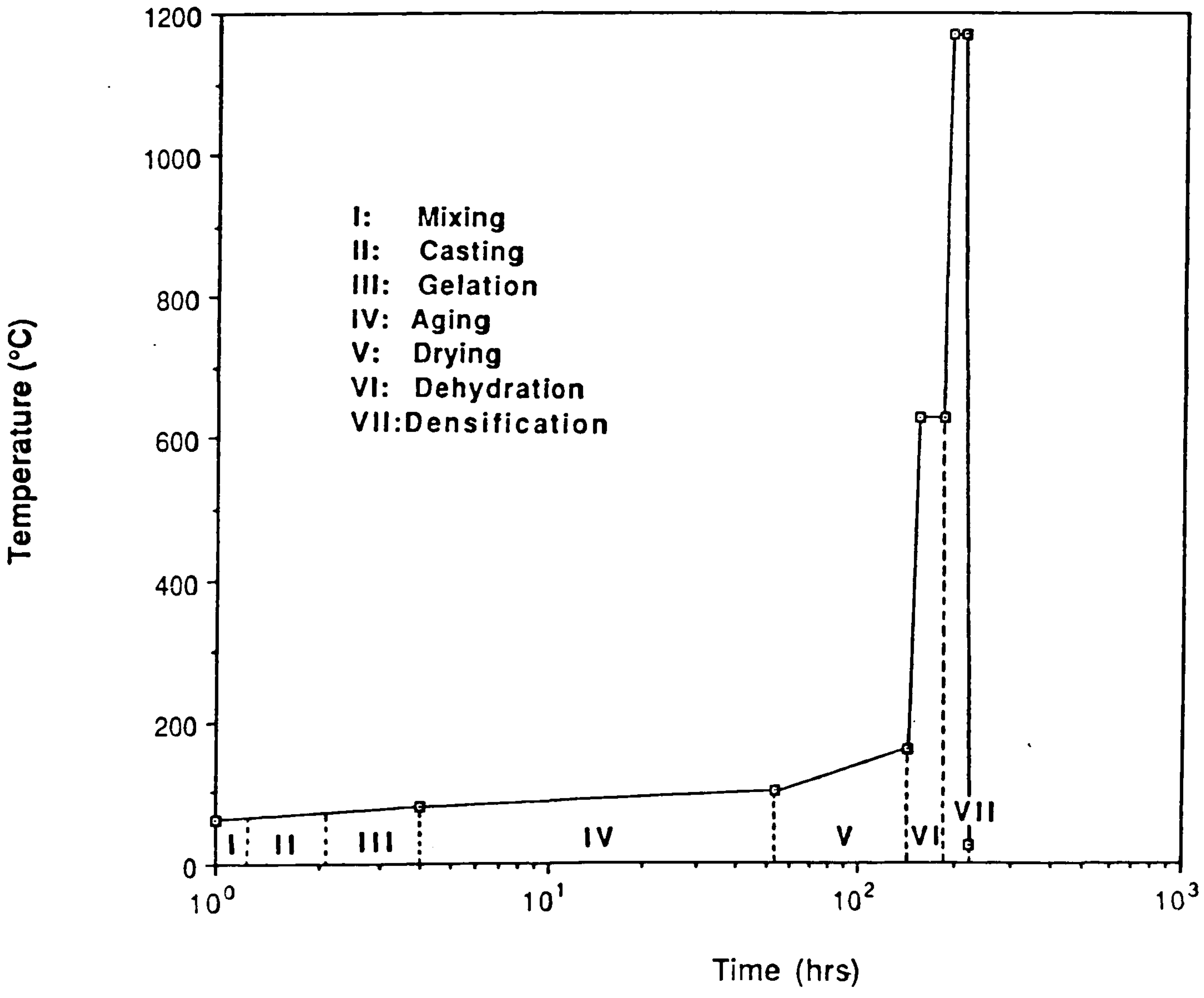

DENSITY
% POROSITY
TEMPERATURE (°C)
O
500
A
B
C
D
E
F
T_D
A
SOL
LIQUID
GEL PARTICLE
B
GEL
C
LIQUID
NECKING
AGED GEL
D
PORE NO LIQUID
DRIED GEL
E
PORE
PARTIALLY DENSIFIED GEL
F
GLASS
PORE
OBJECTIVE
Strength
Surface Area
PHYSICAL PROPERTIES
% POROSITY

Figure 1B, Gel-Silica Glass Process Sequence



A summary of the technical status of Sol-Gel Derived Silica (GELSIL™) optics follows:

TECHNICAL STATUS
OF
SOL-GEL DERIVED SILICA (GELSIL™) OPTICS

Sol-gel derived ultrapure silica (GELSIL™) optics have been shown by comparative analyses at 7 laboratories to have several important physical properties that are superior to any optical glass now on the market. These improved physical properties offer important technical advantages for pure silica GELSIL™ optical products over and above the projected advantages of substantially lower production costs for the sol-gel process and the ability to form near net-shape optics. These advantages are a result of the markedly higher purity of GELSIL™ optics. It is the use of ultrahigh purity chemical precursors and substantially lower processing temperatures which make it possible to achieve ultrahigh purities (Fig. 1B).

The laboratories performing comparative tests of GELSIL™ pilot plant samples and control commercial silica samples are: University of Florida Advanced Materials Research Center, Orton Foundation, Pennsylvania State University, Naval China lake Weapons Center, University of Arizona Optical Science Center, Corning Glass Works, and Glass Fab Inc., Rochester N.Y.

Results of these studies show that the optical transmission of GELSIL™ is markedly superior to commercial (Types I, II and III) optical silicas in the Vacuum Ultraviolet (VUV), the Ultraviolet (UV), Visible (Vis), Near Infrared (NIR), and Infrared (IR), see Figs. 2, 3, 4 and Table 1.

Thus, GELSIL™ optics provide for the first time a lens or window material that has excellent transmission in all five regions of the optical spectrum. In fact, GELSIL™ is close to theoretical limit of cutoff in the UV, which is

Figure 2. Vacuum Ultraviolet Transmission of Optical Silicas

Sample Thickness: 3 mm

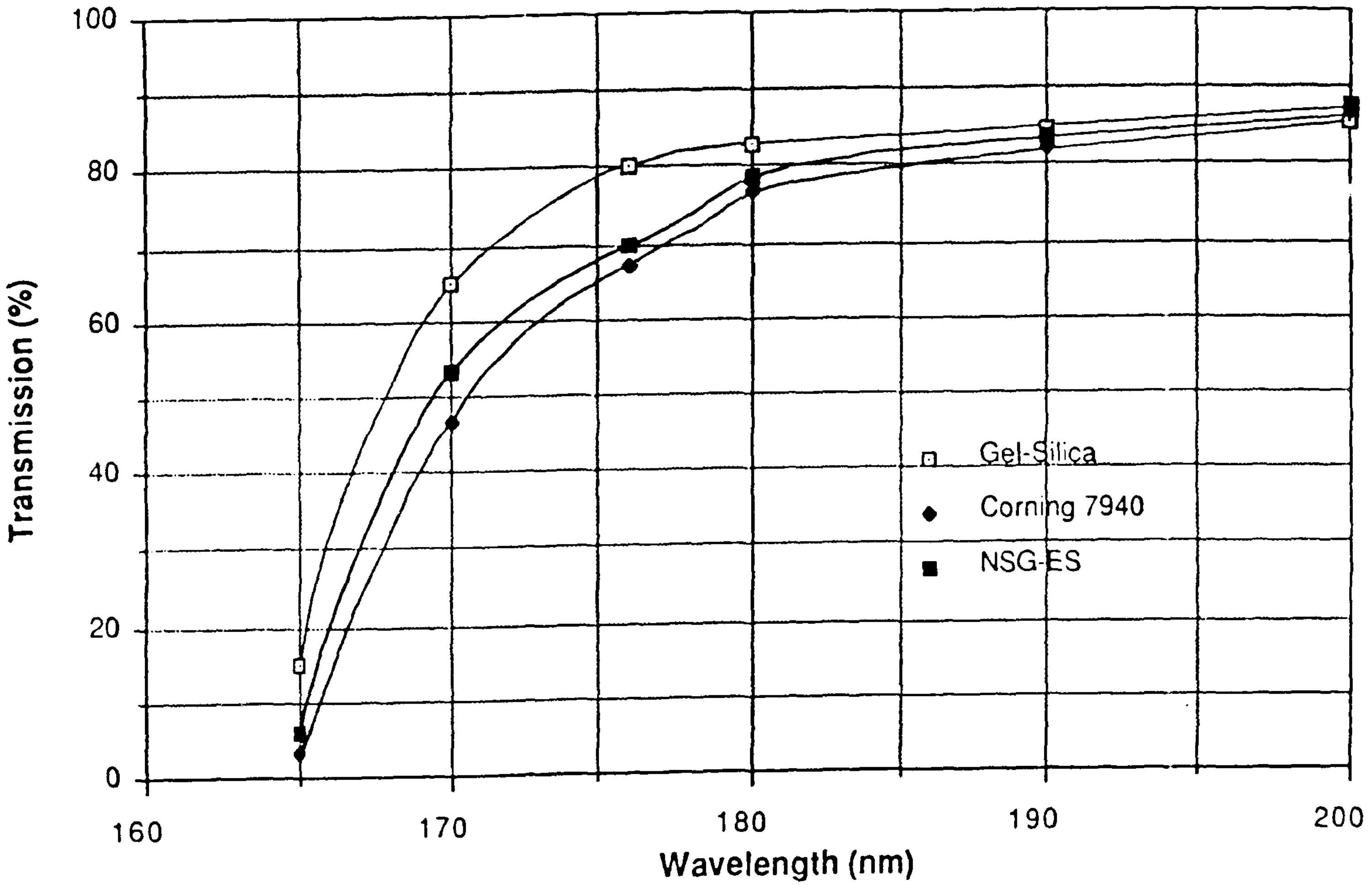


Figure 3. UV-VIS-NIR Transmission of Optical Silicas

Sample Thickness: 3 mm

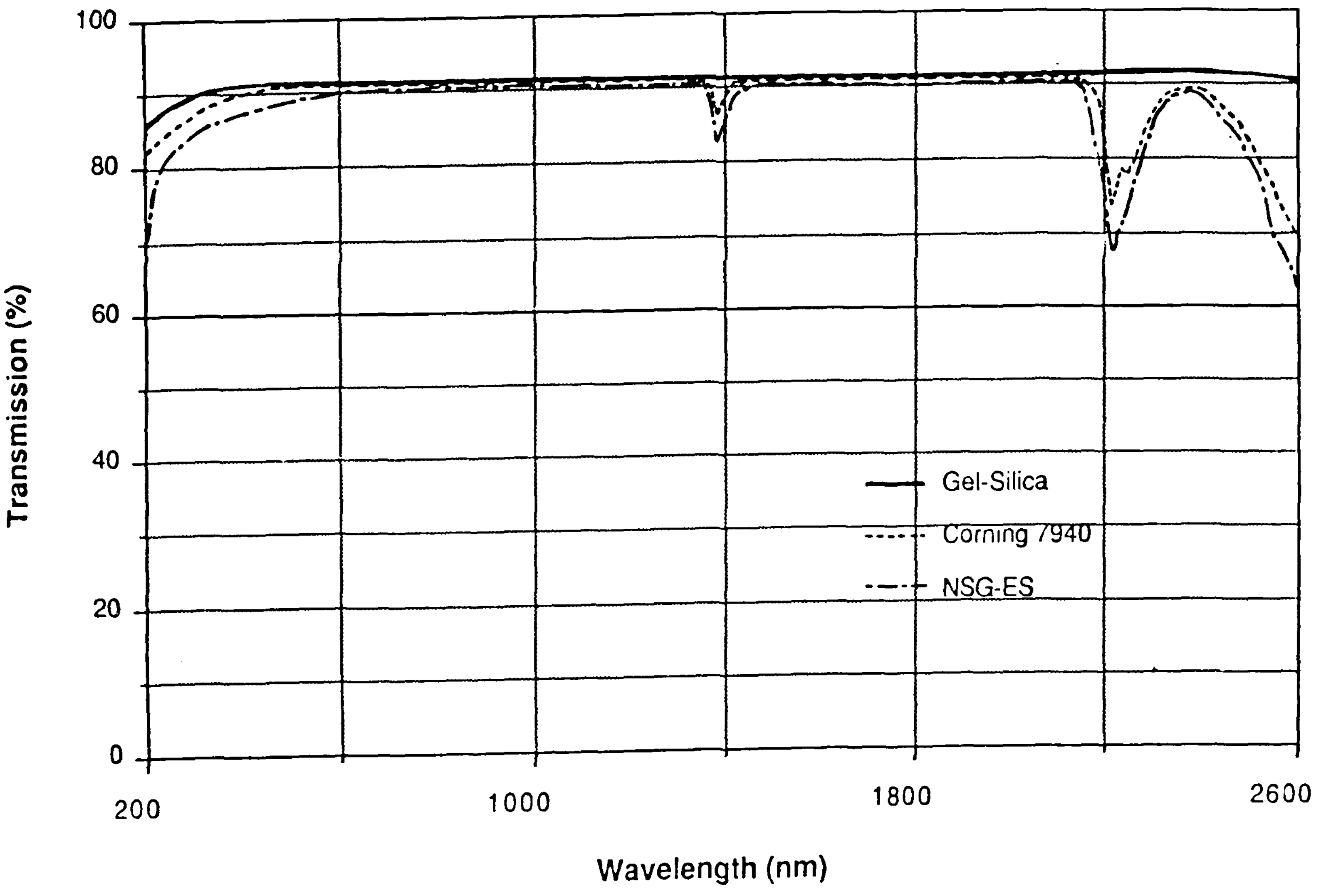


Figure 4. Infrared Transmission of Optical Silicas

Sample Thickness: 3 mm

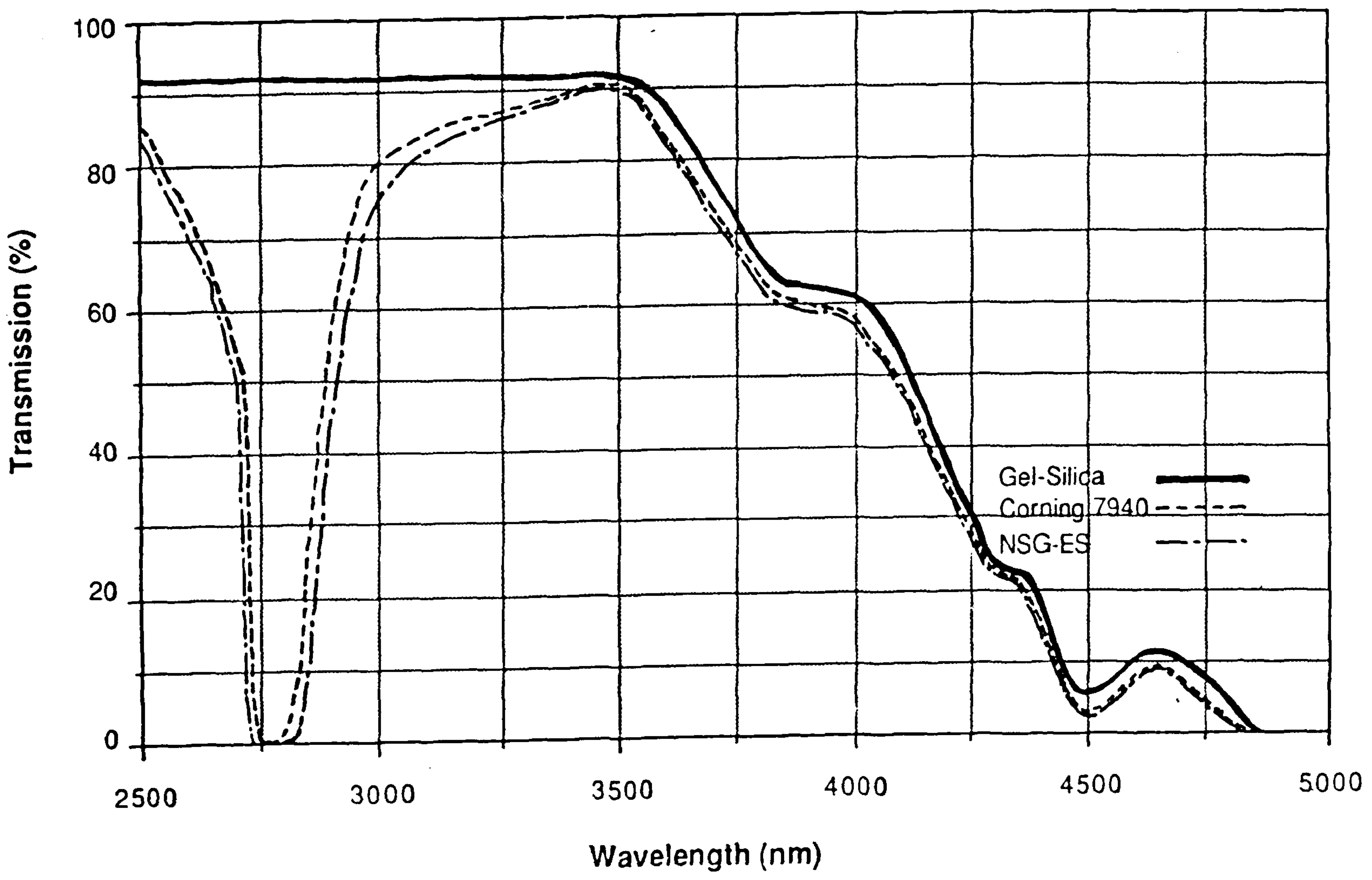


Table 1

SAMPLE ID No.	TRANSMISSION (PER CENT) at WAVELENGTHS OF: 165 nm	170 nm	176 nm	180 nm	190 nm	200 nm
GEL GLASS TEST SAMPLES 3 MM THICK:						
Q 27	13.9 %	65.0 %	80.0 %	83.0 %	84.5 %	85.5 %
N 34	14.0 %	63.0 %	78.0 %	80.5 %	82.5%	83.5 %
P 37	15 .0%	64.0 %	78.5 %	80 5 %	83.0 %	84.0 %
Corning # 7940 Control Sample, 2mm thick:						
CGW-2 (a)	08.0 %	60.0 %	76.0 %	83 0 %	88.0 %	91 0 %
Corning # 7940 Control Sample, Converted to 3 mm thickness:						
CGW-2 (a)	03.0 %	47.0 %	67.0 %	77.0 %	82.5 %	87 0 %
FORM REFERENCE, REFLECTION LOSS PER SINGLE SURFACE:						
R Loss (b)	05.7 %	05.5 %	05.3 %	05.1 %	04.9 %	04 7 %

NOTES:

a) As noted, the Corning #7940 samle measured was 2 mm thick compared to the 3 mm thick gel-glass test samples. This data was converted to 3 mm thickness for comparison.

b) Reflection losses shown are based on published data for fused silica available from Glass Fab Inc and is *presented for reference* only.

especially important for the greatly expanding interest in using UV frequencies in optical communications and microelectric photo masks. Figure 2 and Table 1 shows that at 165 nm GELSIL™ has 5 times the transmittance of Corning 7940 optical silica.

Another marked advantage of GELSIL™ optics over other commercial silicas is a higher index of refraction (n) and lower dispersion (dn/dl), (Fig. 5). The index of refraction of GELSIL™ in fact can be varied by altering the thermal processing schedule, (Fig. 6).

Consequently, it is possible to produce a wide range of waveguides and optical elements using GELSIL™ with much greater control than is possible with traditional silica optics which require chemical doping.

The GELSIL™ process also results in near net shape optics which require almost no grinding or polishing even when complex configurations are produced, such as aspheric optics or lightweight structures. The homogeneity is equivalent or superior to the best fumed silica optics or hand-selected fused quartz optics, (Fig. 7)

In addition to superior optical transmittance, GELSIL™ samples have been shown by comparative analyses at 4 laboratories to have a uniquely low coefficient of thermal expansion (CTE) and nearly zero temperature dependence of CTE, CTE/dT=0. These results, along with those of a number of other currently sold optical materials, are shown in Fig. 8. The importance of this characteristic is that GELSIL™ optical components exposed to high temperature, or varying temperature, or large optical power densities will expand or contract very little.

Therefore, performance limits of the optical components can be very much higher than are now presently available. Improved thermal performance

Figure 5. Dispersion Data Comparison of Optical Silicas

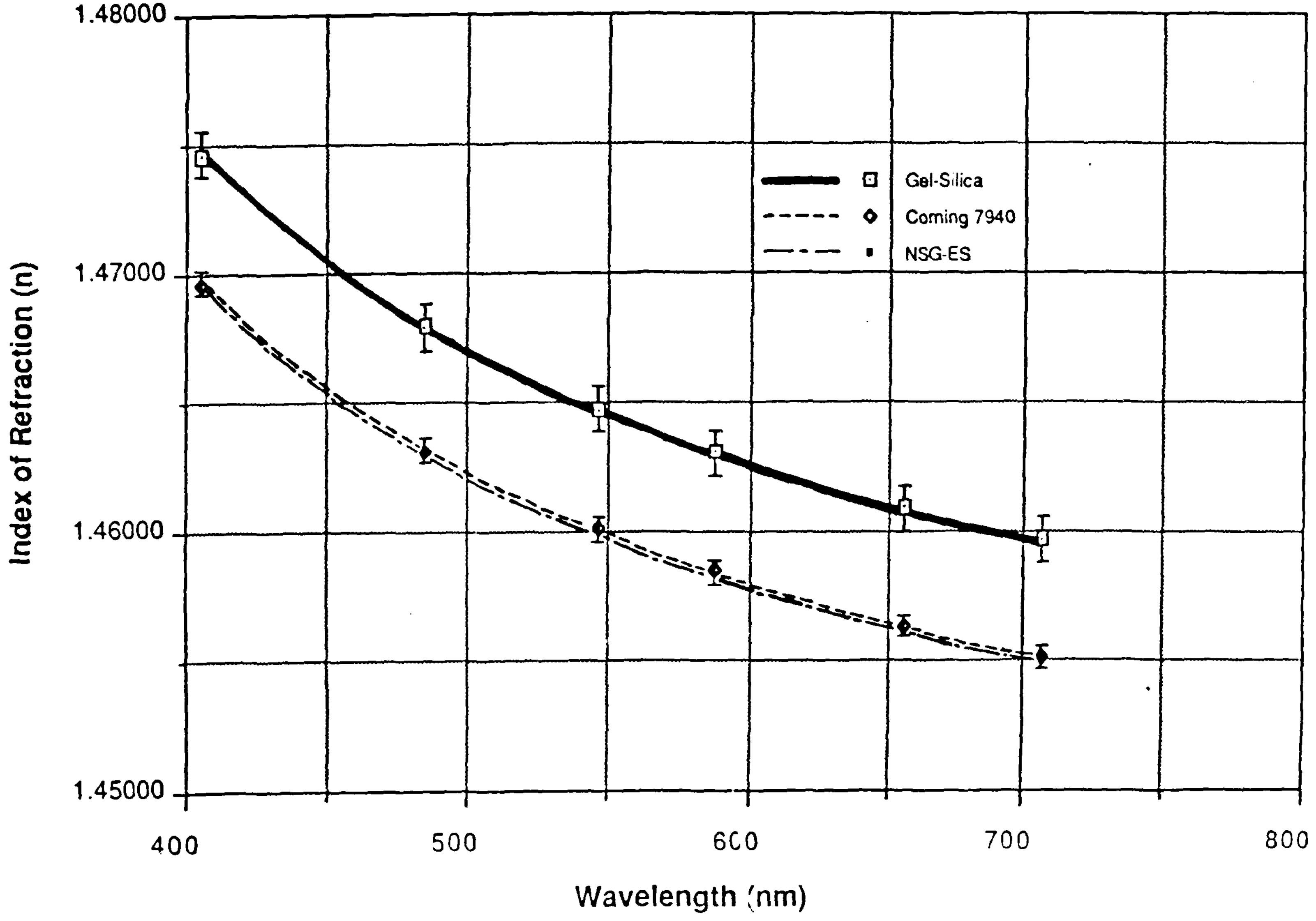


Figure 6

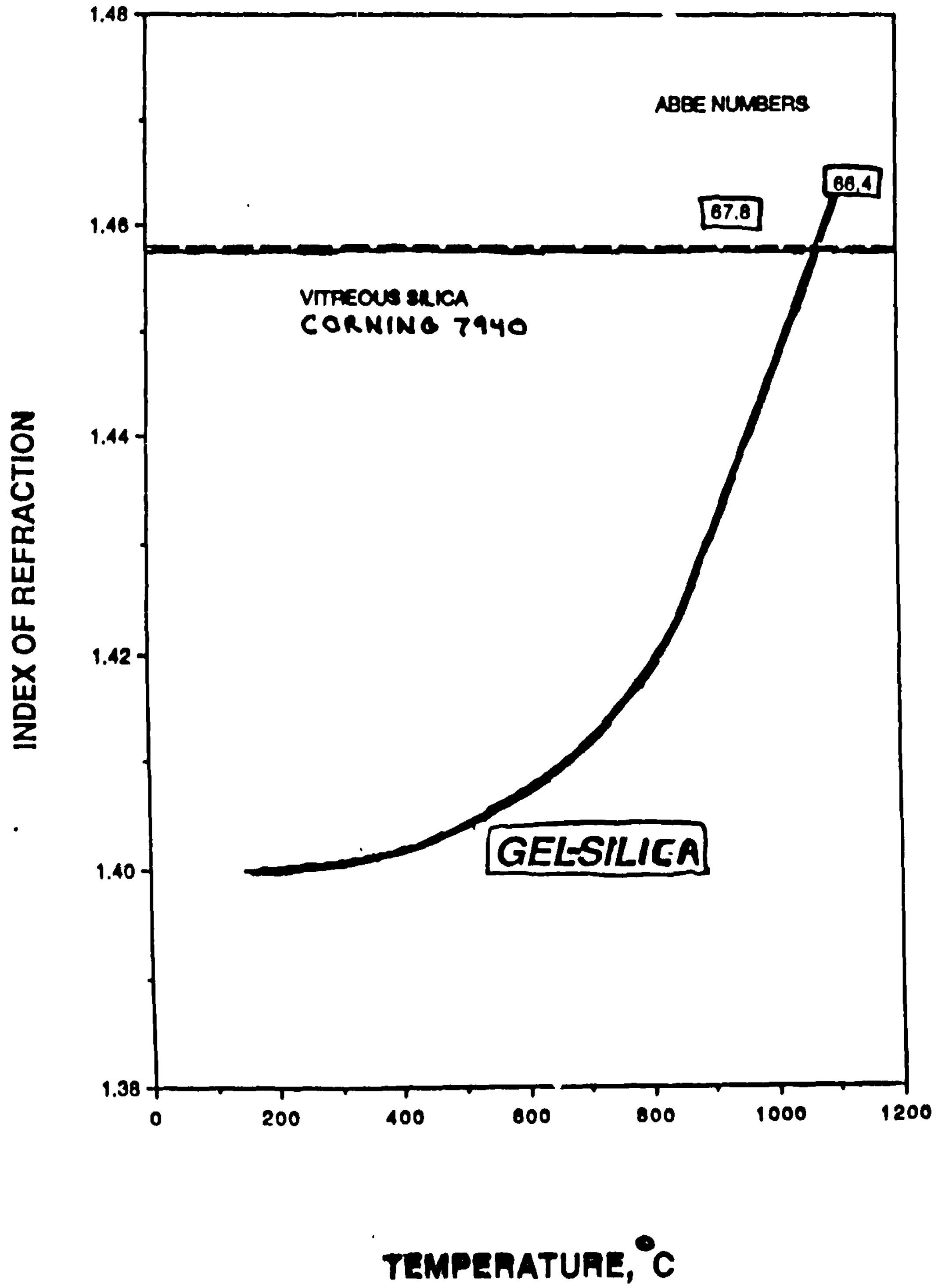
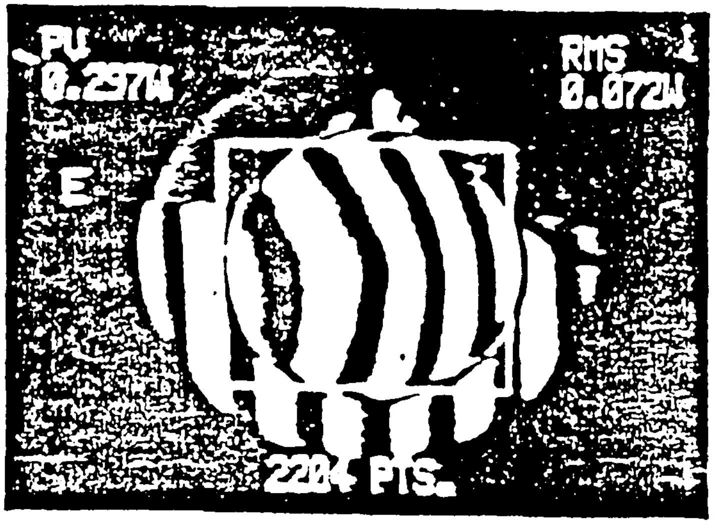
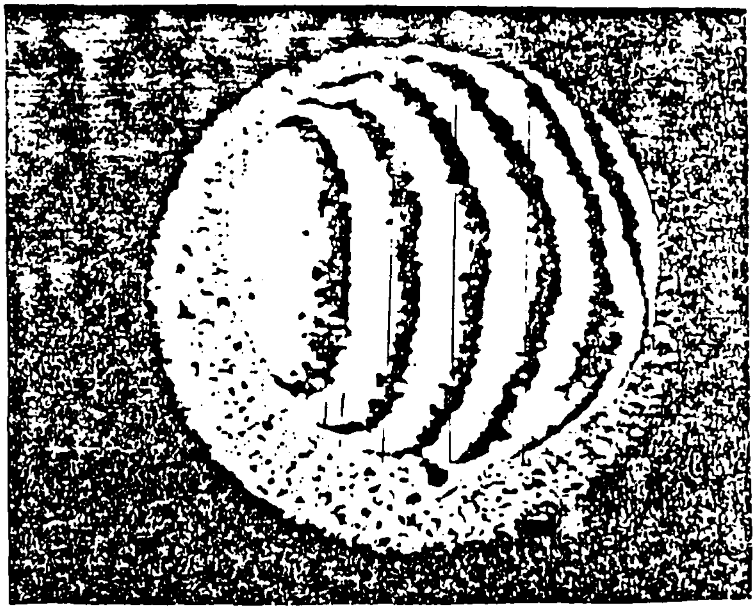

ABBE NUMBERS
66.4
67.8
VITREOUS SILICA
CORNING 7940
GEL-SILICA
INDEX OF REFRACTION
1.48
1.46
1.44
1.42
1.40
1.38
0
200
400
600
800
1000
1200
TEMPERATURE, °C

Figure 7. **TEST OF HOMOGENEITY USING ZYGO INTERFEROMETRY**

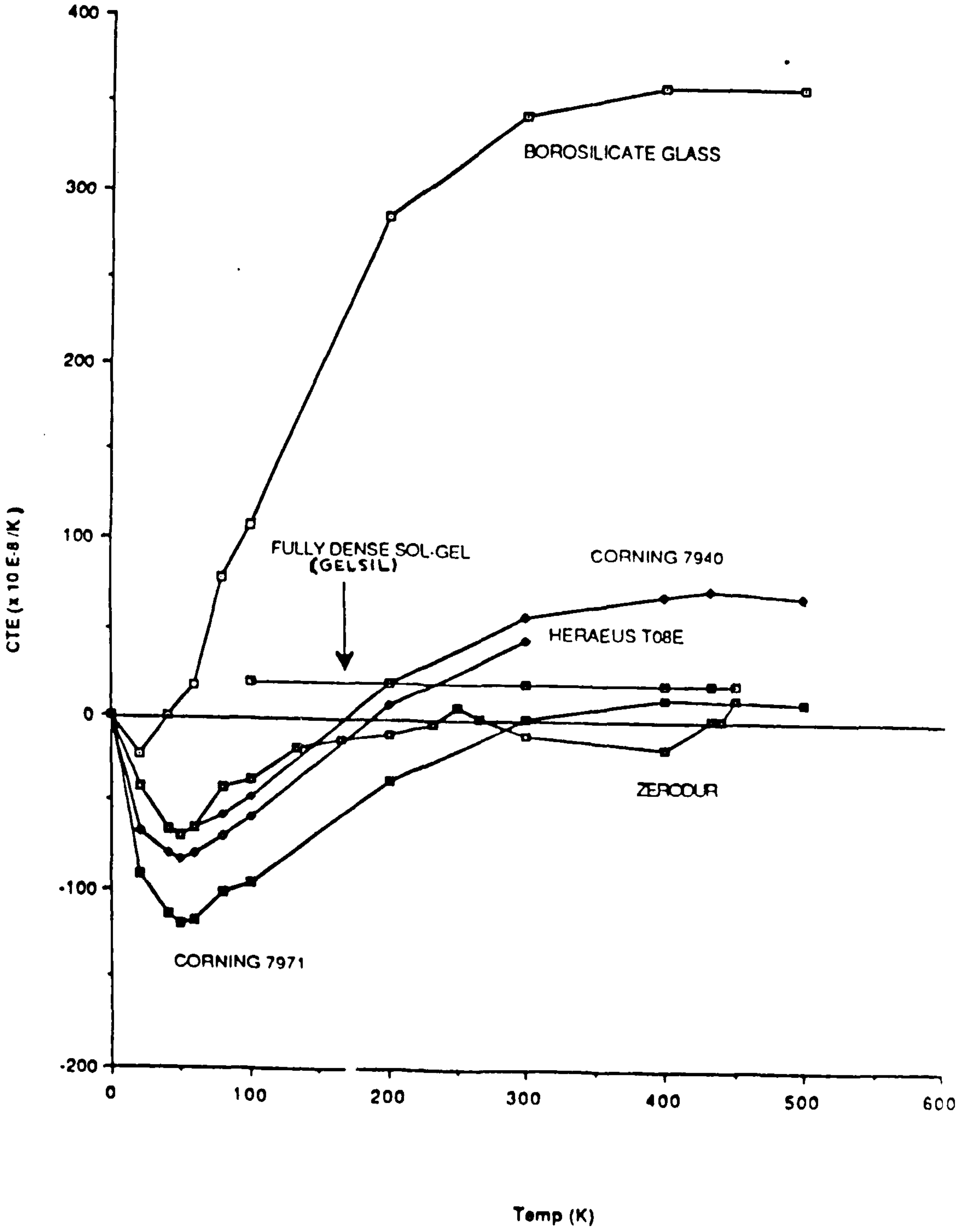


CORNING 7940
CONTROL SAMPLE



GELSIL™
FOURTH GENERATION
PROCESS
03/05/87

Figure 8 Coefficient of Thermal Expansion of Gel Silica Compare With Other Fused Glasses

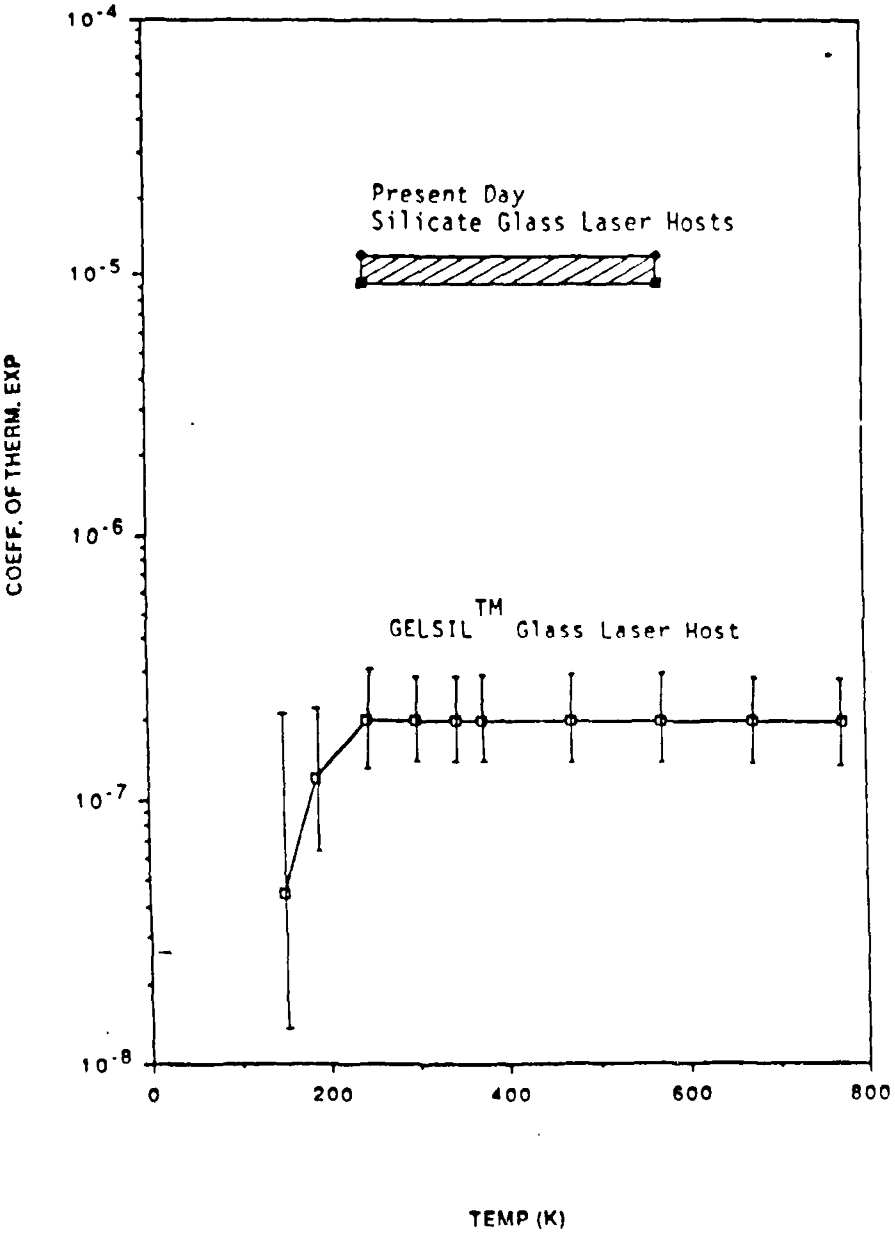


combined with lower optical absorbance, due to superior transmittance, means that overall operating thresholds for many optical components can be increased, cooling requirements can be decreased, size of components can be increased, etc. The net effect should be a broad range of DOD applications for GELSIL™ Optics.

Recent studies in GELTECH, Inc. and University of Florida AMRC laboratories have also resulted in a proprietary process for doping GELSIL™ optical components with a very broad range of elements, such as the rare earth oxides and transition metal oxides. A similar process has been developed for impregnation of porous GELSIL™ with multifunctional polymers.

The GELTECH doping process makes it possible to produce a highly homogeneous distribution of additives in a dense silica matrix. Thus, the important advantages of GELSIL™ pure silica passive optics summarized above can be expanded to include potential uses in a broad range of optical filters and in active optical components, such as glass lasers.

Theoretical calculations show that this development should lead to very large improvements in solid state glass lasers. Figure 9 compares the CTE of the doped GELSIL™ laser material with that of the commercially available silicate glass laser hosts. There is a factor of 50 better CTE characteristics for the GELSIL™ laser host. Many other advantageous physical characteristics of the GELSIL™ host have now been established as well. An active research program is underway in GELTECH laboratories to produce a solid state GELSIL™ laser. Additional research is in progress to use the same technical approach to produce solid state tunable lasers. This work is an international collaboration with Dr. Terry King at the University of Manchester, England.



10^-4
10^-5
10^-6
10^-7
10^-8
COEFF. OF THERM. EXP
Present Day
Silicate Glass Laser Hosts
GELSIL TM Glass Laser Host
0
200
400
600
800
TEMP (K)

Figure 9

An important feature of the MIRP is continued collaboration with a number of investigators in other institutions.

Extensive collaboration continues between our sol-gel research program and that of Prof. Jiri Jonas at the University of Illinois, Prof. Robert West at the University of Wisconsin, and Dr. Jean Phalippou at the University of Montpellier, France. A number of manuscripts based upon this interinstitutional research have been published (see Publication List).

During this contract our multidisciplinary team was expanded to include Professor R.W. Gould of the Department of Materials Science and Engineering, University of Florida. Professor Gould initiated a collaboration with the X-ray facility at Oak Ridge National Laboratory for x-ray small angle scattering leading to several publications on gel processing and ultrastructure characterization. He also is setting up a precision wide angle x-ray diffraction lab at the University of Florida for gel structure studies.

During this contract Project B has been included a number of investigations of ceramic-ceramic composites, led by Prof. D. E. Clark, and has also launched new sol-gel derived refractory ceramic coatings. The following schematics illustrate the technical approach taken in this new area of sol-gel ceramic coatings.

Figure 10 presents a comprehensive overview of Professor Clark's coatings research on carbon/carbon composites. The long-term goal is shown in the bottom right hand corner. This involves deposition of a protective coating of chemically derived hafnia (HfO_2) reinforced with SiC whiskers. The role of hafnia is to provide the high temperature oxidation protection, while the role of SiC is to provide reinforcement at high temperatures. Shown in the left column is the model system where we use graphite substrates and coat them with

MIRP CHEMICALLY DERIVED COATINGS RESEARCH

PERFORMANCE VERSUS MATERIALS STSTEM

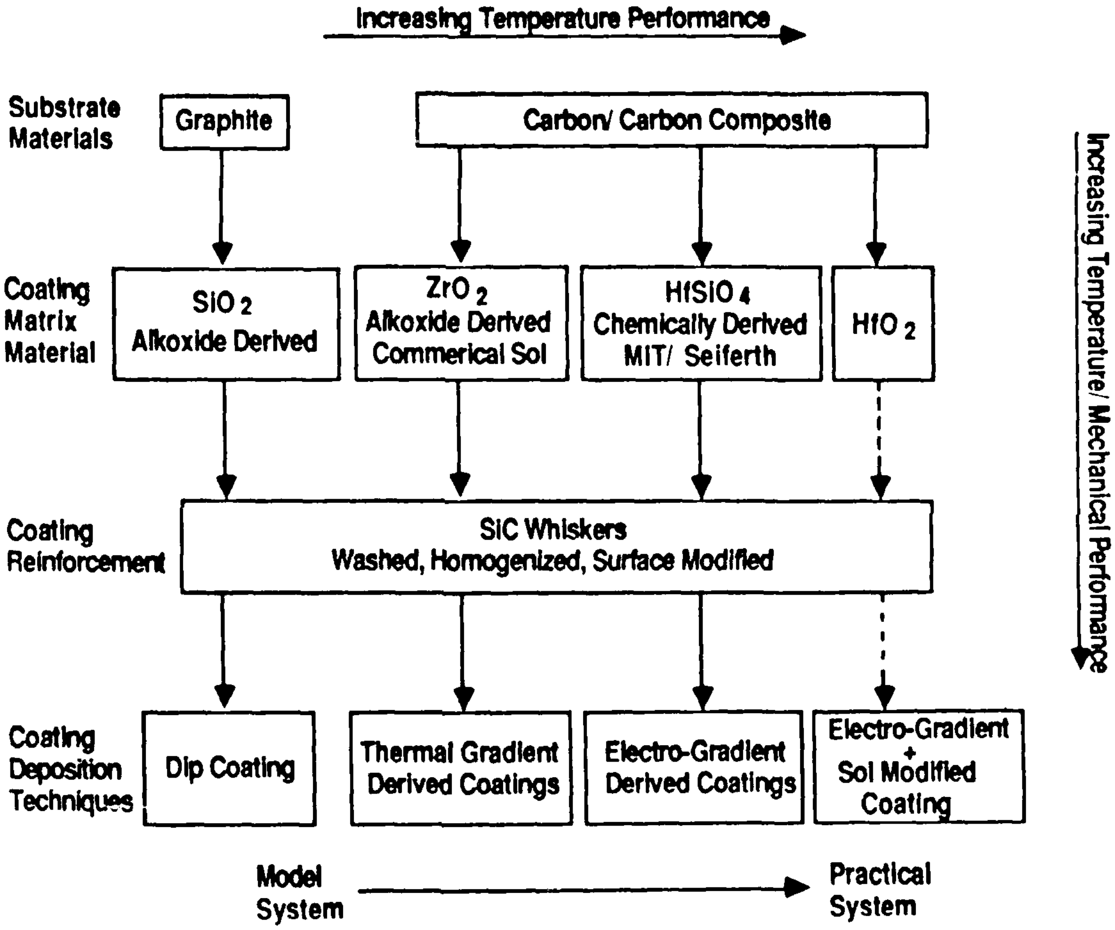
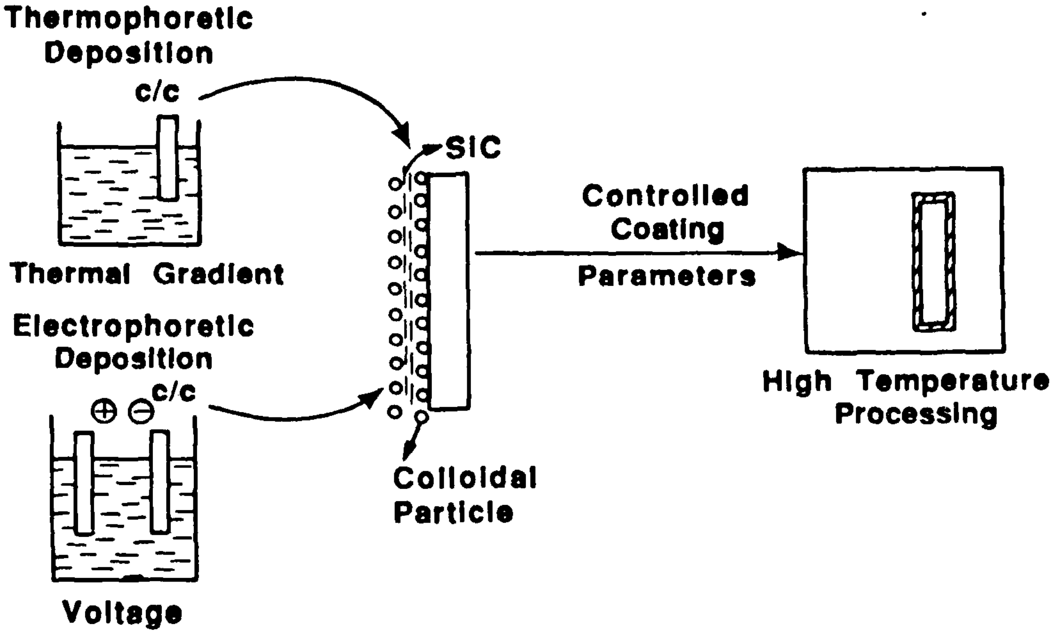


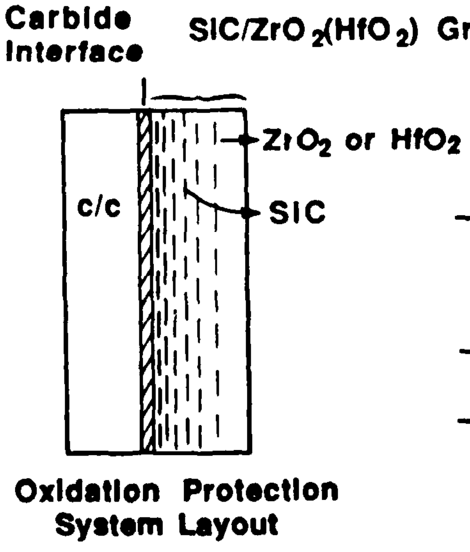
Figure 10.

oxides such as SiO_2 and Al_2O_3. The reason for using graphite is twofold: 1) C/C composite samples are expensive, and 2) preparation of experimental samples from C/C substrates is difficult due to the anisotropy of the fiber weave. Note that as you move across the diagram from left to right and down the diagram from top to bottom the degree of coating complexity increases as does the expected performance of the coating.

The major focus areas are (Figs. 11 and 12): 1) Development of an understanding of the basic chemistry of composite coatings and 2) Development of an understanding of how the nano/micro structures can be controlled through specialized deposition methods. This latter focus area is illustrated in Fig. 12. The sols of interest for matrix, SiO_2, Al_2O_3, ZrO_2, and HfO_2, all contain charged colloids in suspension. The surface chemistry of these colloids can be modified and controlled by a number of methods. We have selected pH as a primary method for controlling surface charge on the colloids. The colloids in the matrix sol are positively charged at low pH and can be driven towards a negative electrode, such as superalloys or carbon/carbon. Upon impact, the colloids adhere to the electrode and form a layer. The structure of this layer (i.e. porosity, density, etc.) can be controlled by the pH. The lower the PH the higher the charge on the colloids and the greater their impact velocity. Note that at a certain pH the surface charge will become zero and the colloids will not be plated onto the substrate. The versatility of this approach is that when a reinforcement such as SiC whiskers is added to the sol, these have a different response to pH. This difference permits a wide variety of coatings to be produced ranging from pure matrix to a "graded" layer containing both matrix and reinforcement. Furthermore, the charge

CHEMICALLY DERIVED OXIDATION PROTECTION COATINGS





- Gradient Coating of SiC/ ZrO_2 or HfO_2 Produced by Controlling Surface Charge of Colloidal Particles in Sol and SiC Whisker
- SiC Provides Oxidation Protection<2500° F
- ZrO_2, HfO_2 (Stabilized) Provides Oxidation Protection>2500° F

Figure 11.

CONTROLLED NANO/MICRO STRUCTURES OF CHEMICALLY DERIVED COATINGS

SURFACE MODIFIED COATINGS BY:

1. **Preferred Orientation of Whiskers**
2. **Layering**

Obtained by Controlling Sol Chemistry
(i.e. pH, Electrolyte Concentration)

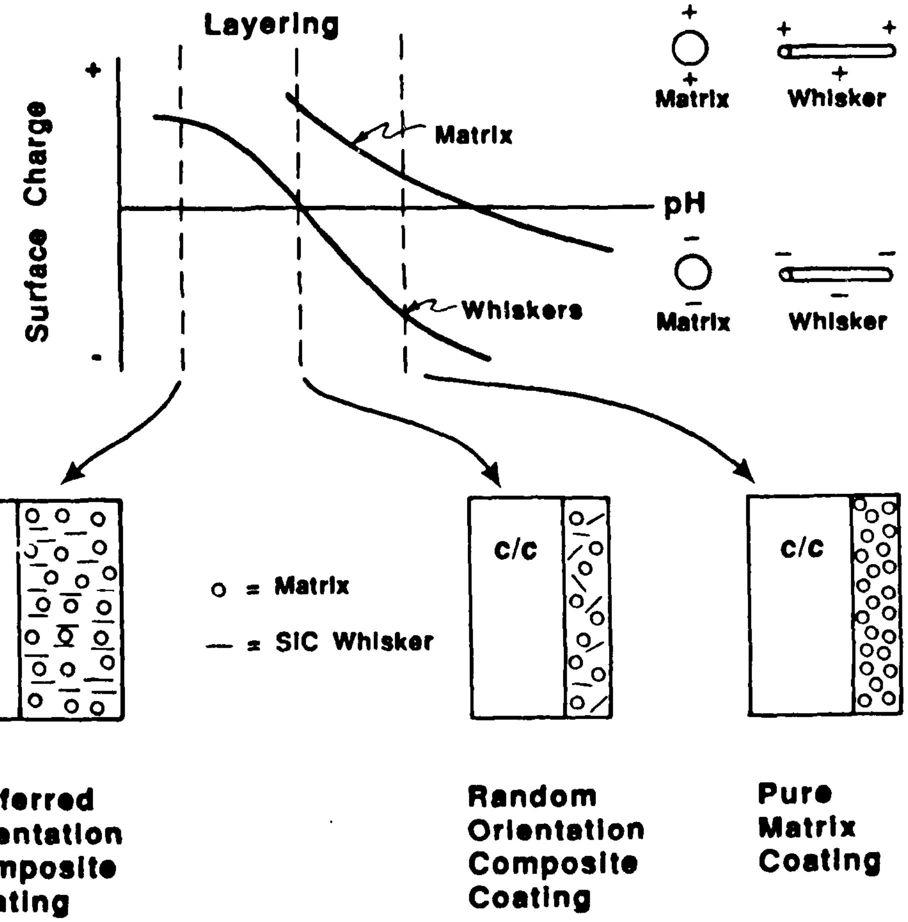


Figure 12.

distribution on the asymmetrical whiskers permits the deposition of preferred orientation composite coatings.

Figure 12 illustrates the electrophoretic and thermophoretic methods for depositing composite coatings onto a carbon/carbon substrate.

In the electrophoretic method, the carbon/carbon electrode is made negative in order to attract the positively charged matrix colloids and SiC whiskers. The driving force for deposition is the electric gradient that exists between the electrode and sol which can be modified and controlled by pH.

In the thermophoretic method, the temperature of the carbon/carbon electrode is reduced relative to the sol and the driving force for deposition is T. This results in very thin tenaciously bonded coatings.

Shown on the bottom of this figure is a gradient coating where the concentration of SiC whiskers is varied throughout the thickness. The purpose of the gradient coating, which is produced electrophoretically, is to accommodate mismatches in expansion coefficients between the C/C and coating.

Our third approach to ultrastructure processing, Project C, is based in part upon the discovery of Prof. West and colleagues at the University of Wisconsin that silane precursors, such as polysilastyrene (PSS), can be thermally decomposed to form SiC. Samples of high molecular weight polysilastyrene provided by Prof. West and PSS oligimers made at 3M Co. in collaboration with Dr. Robin Sinclair, and other polysilanes obtained from Kurt Schilling (Union Carbide) and Barry Arkles (Petrarch Co.) have been studied to determine the functional range for polymer crosslinking and the pyrolysis conditions necessary to control formation of SiC. The effects of extended UV radiation, atmosphere during irradiation, molecular end groups on the silane, and pyrolysis atmosphere and thermal schedules have been examined. A number of manuscripts have been published describing successful chemical means for crosslinking the polysilanes and impregnating polysilanes into sol-gel derived silica monoliths. After pyrolysis, superior hardness to weight ratios are obtained for these ultrastructural composites due to SiC reinforcement. Several patents have been filed, based upon this work. This work involves primarily the efforts of Dr. B. I. Lee, a Ph.D. graduate of the MIRP, who is now a faculty member in Ceramic Engineering at Clemson University.

Our efforts to understand and control the uniquely attractive electronic properties of SiC (Project D) have led to significant advances in measuring and interpreting the noise spectrum and transport properties of SiC single crystals. This work, under the direction of Prof. Gijs Bosman and Prof. C. Van Vliet in Electrical Engineering has been extended to verify the general theory of space charged limited (SCL) flow of semiconductors developed by Prof. Van Vliet several years ago. A number of papers have been published (see Publication List). A major review of the electronic characteristics of SiC was also published in the Annual Review of Materials Science. This review provides a theoretical basis for design of new electronic and optical devices utilizing siC, assuming polytypes can be controlled during process. This effort is now being extended to include amorphous Si SCL flow in Schottky barrier diodes as well.

LIST OF PUBLICATIONS

"Use of Drying Control Chemical Additives (DCCAs) in Producing Gel Monoliths," L. L. Hench in Glass...Current Issues, A. F. Wright and J. Dupuy, eds., Martinus Nijhoff Publishers, Dordrecht, The Netherlands, 1985, pp. 259-262.

"NMR Raman Study of the Effect of Additives on the Sol-Gel Process," I. Artaki, M. Bradley, T. W. Zerda, J. Jonas, G. Orcel and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 73-80.

"Comparative Pore Distribution Analysis of Sol-Gel Derived Silica," S. Wallace and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 148-156.

"Physical Properties of Partially Densified SiO_2 Gels," S. Park and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 168-172.

"Sol-Gel Derived Silica Optical Filters," S. H. Wang and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 201-207.

"Processing and Structural Properties of Li_2O-Al_2O_3-TiO_2-SiO_2 Gels," G. Orcel and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 224-230.

"Physical-Chemical and Biochemical Factors in Silica Sol-Gels," L. L. Hench and G. Orcel, J. Non-Crystalline Solids 82 (1986) 1-10.

"Processing and Structural Evolution of (xLi_2O $(1-x)Na_2O$) Al_2O_3 $2SiO_2$ Gels," G. Orcel, J. Phalippou, and L. L. Hench, J. Non-Crystalline Solids 82 (1986) 301-306.

"Structural Changes of Silica Xerogels During Low Temperature Dehydration," G. Orcel, J. Phalippou and L. L. Hench, J. Non-Crystalline Solids 88 (1986) 114-130.

"Effect of Formamide Additive on the Chemistry of Silica Sol-Gels, Part I: NMR of Silica Hydrolysis," G. Orcel and L. L. Hench, J. Non-Crystalline Solids 79 (1986) 177-194.

"Sol-Gel Glass," L. L. Hench, McGraw Hill Yearbook of Science and Technology, 1987, pp. 221-223.

"Polarized Infrared Reflection Spectroscopy of Single Crystal Lithia-Silicates and Quartz," W. J. McCracken, W. B. Person, and L. L. Hench, J. of Materials Science 20 (1985) 3853-3864.

"Sol-Gel Derived Ceramic Matrix Composites," D. E. Clark, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley & Sons. 1986, 237-246.

"Processing of Sol-Gel Derived Doped Powders and Substrates," K. W. Wistrom and D. E. Clark, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley & Sons. 1986, 272-277.

"Thermophoretic and Electrophoretic Deposition of Sol-Gel Composite Coatings," W. J. Dalzell and D. E. Clark, Ceramic Engineering and Science Proceedings, 7[7-8], (1986) 1014-1026.

"Use of FT-IRRS for Characterizing Thermal Stability of SiC Whiskers and Composites," G. P. LaTorre, R. A. Stokell, R. H. Krabill and D. E. Clark, Ceramic Engineering and Science Proceedings, 7[7-8], (1986) 933-944.

"Effect of Surface Hydration on Polymer Adsorption," Brij M. Moudgil and Yeu-Chyi Cheng, Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley & Sons. 1986, 550-554.

"Electrophoretic Behavior and Surface Reactions of Sol-Gel Derived Alumina," B. I. Lee and L. L. Hench, Colloids and Surfaces 23 (1987) 211-229.

"Crosslinking and Pyrolysis of Silane Precursors for Silicon Carbide," B. I. Lee and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 345-353.

"Silicon Carbide/Silica Gel Matrix Composites," B. I. Lee and L. L. Hench in Science of Ceramic Chemical Processing, L. L. Hench and D. R. Ulrich, eds., J. Wiley and Sons, New York, NY, 1986, pp. 231-236.

"Silicon Carbide/Silica Molecular Composites," B. I. Lee and L. L. Hench in Ceramic Engineering and Sciences Proceedings, Am. Ceram. Soc., Columbus, Ohio, July-August 1986, pp. 994-997.

"Observation of Single Carrier Space-Charge Limited Flow in Nitrogen-Doped α-Silicon Carbide. I. I-V Characteristics and Impedance," S. Tehrani, J. S. Kim, L. L. Hench, C. M. Van Vliet and G. Bosman, J. Appl. Phys. 58[4] (1985) 1562-1570.

"Observation of Single Carrier Space-Charge Limited Flow in Nitrogen-Doped α-Silicon Carbide. II. I-V Electrical Noise," S. Tehrani, L. L. Hench, C. M. Van Vliet and G. Bosman, J. Appl. Phys. 58[4] (1985) 1572-1577.

"The Role of Chemical Additives in Sol-Gel Processing," L. L. Hench, G. Orcel and J. L. Nogues in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 35-47.

"SAXS Study of Silica Sols and Gels," G. Orcel, R. W. Gould and L. L. Hench in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 289-294.

"Processing and Properties of $xSiO_2-(1-x)Al_2O_3$ Gels," G. Orcel, J. Phalippou, and L. L. Hench, Rev. Int. Hautes Temper. Refract. Fe. 22 (1985) 185-190.

"Optical Properties of Gel-Silica Glasses," Shi-Ho Wang, Candace Campbell and L. L. Hench to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Dielectric Relaxation Analysis of Gel Drying, S. Wallace and L. L. Hench to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Sol-Gel Coatings on Carbon/Carbon Composites," S. M. Sim, R. H. Krabill, W. J. Dalzell, Jr., P-Y. Chu, and D. E. Clark in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 647-652.

"Drying Behavior of Sol-Gel Derived Al_2O_3 and Al_2O_3-SiC Composites," R. H. Krabill and D. E. Clark in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 641-646.

"Chemically Derived Refractory Coatings," S. M. Sim. P-Y. Chu, R. H. Krabill and D. E. Clark, to be published in the Proceedings of the 3rd Ultrastructure Conference on Ceramics, Glasses and Composites, San Diego, CA, February 23-27, 1987.

"Surface Charge of Sol-Gel Derived Aluminas as a Function of Calcination Temperature," Burtrand I. Lee and Larry L. Hench, Particulate Science and Technology 4 (1986) 213-223.

"Silicon Carbide from Organosilanes and Application in Silica Gel Glass Composites," B. I. Lee and L. L. Hench in Better Ceramics Through Chemistry II, C. Jeffrey Brinker, David E. Clark and Donald R. Ulrich, eds., Vol. 73, Materials Research Society, Pittsburgh, PA, 1986, pp. 815-822.

"Observation of Single Carrier Space-Charge-Limited Flow in Nitrogen Doped α-Silicon Carbide. III. Computer Calculations," S. Tehrani, G. Bosman, L. L. Hench and C. M. Van Vliet, J. Appl. Physics 60[7] (1986) 2386-2395.

"New Perspectives of Silicon Carbide: An Overview, With Special Emphasis on Noise and Space-Charge-Limited Flow," Carolyn M. Van Vliet, Gijs Bosman, and Larry L. Hench, Ann. Rev. Mater. Sci. 18 (1988) 381-421.

"Gel-Silica Optics," L. L. Hench, S. H. Wang, and J. L. Nogues, in Multifunctional Materials, Vol. 878, Robert L. Gunshor, ed., SPIE, Bellingham, WA, 1988, pp. 76-85.

"Correlations Between Processing Parameters, Ultrastructure, and Strength of Gel-Silica," J. K. West, R. Nikles, and G. LaTorre, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Physical Properties of Dried Na_2O-SiO_2 Monoliths," R. Li and L. L. Hench, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Physical and Structural Evolution of Sol-Gel Derived TiO_2-SiO_2 Glasses," Y. C. Cheng and L. L. Hench, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Dielectric Relaxation Analysis of Water Adsorption in Sol-Gel Derived Silica Gel Monoliths, S. Wallace and L. L. Hench to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

"Preparation and Characterization of Monolithic Si-Ce-O Gels," A. Sivade, G. Orcel, L. L. Hench, J. Bouaziz, R. Sempere, D. Bourret, presented at the 40th Pacific Coast Regional Meeting of the American Ceramic Society, San Diego, CA, Nov. 3, 1986.

"Gel-Silica Waveguides," R. V. Ramaswamy, T. Chia, R. Srivastava, A. Miliou and J. West, in Multifunctional Materials, Vol. 878, Robert L. Gunshor, ed., SPIE, Bellingham, WA, 1988, pp. 86-93.

"Coating Porous Substrates by the Sol-Gel Method," P-Y. Chu and D. E. Clark, presented at the 89th Annual Meeting and Exposition of the American Ceramic Society, Pittsburgh, PA, April 27, 1987.

"Molecular Composites of SiC/SiO_2, SiC/Al_2O_3, and SiC/TiC," Burtrand I. Lee and Larry L. Hench, Am. Ceram. Soc. Bull. 66[10] (1987) 1432-1485.

"Comparison of Polysilastyrene with Polycarbosilane as a Precursor to Silicon Carbide," B. I. Lee, presented at the Fiber Tex-87, Nov. 3-5, 1987, in press.

"Mechanical Properties of Partially Densified SiC/SiO_2 Gel Matrix Composites," B. I. Lee and L. L. Hench, in Ceramic Engineering and Science Proceedings, Am. Ceram. Soc., Westerville, Ohio, 8[7-8], 1987, 685.

"Theory and Experiments of 1/f Noise in Schottky-Barrier Diodes Operating in the Thermionic-Emission Mode," Min-Yih Luo, Gijs Bosman, Aldert van der Ziel, and Larry L. Hench, IEEE Transactions of Electron Devices 35[8] (1988) 1351-1356.

"Ceramics and the Challenge of Change," L. L. Hench, Advanced Ceramic Materials 3[3] (1988) 203-206.

"Corrosion of Silicate Glasses: An Overview," L. L. Hench, to be published in the Proceedings of the MRS Spring Meeting, Reno, Nevada, April 5-9, 1988.

LIST OF PATENT APPLICATIONS

1. Drying Control Chemical Additives for Rapid Production of Large Sol-Gel Derived Silicon and Lithium Containing Monoliths
2. Drying Control Chemical Additives for Rapid Production of Large Sol-Gel Derived Silicon-Containing Monoliths
3. Drying Control Chemical Additives for Rapid Production of Large Sol-Gel Derived Silicon, Boron and Sodium Containing Monoliths
4. Method for Rapid production of Large Sol-Gel SiO_2 Containing Monoliths of Silica With and Without Transition Metals and Products
5. Process for Rapid Production of Large Sol-Gel Monoliths Containing Rare Earths and Products
6. Process for Rapid Production of Large Sol-Gel SiO_2 Monoliths Containing Transition Metals and Products
7. Method for Producing Sol-Gel Derived SiO_2/Oxide Powder Composites and Novel Composites
8. Method for Crosslinking of Polysilastyrene and Pyrolyzing to Produce Silicon Carbide Material
9. Method for Making Silica Optical Devices and Devices Produced Thereby
10. Method for Low Temperature Processing of Lightweight SiC/SiO_2 Composites and Products
11. Method of Fabricating Ultraporous Gel Monoliths Having Predetermined Pore Sizes and Products
12. A Process for Rapid Production of Large Sol-Gel Derived Aluminum Containing Monoliths
13. Method for Obtaining an Intermediate Sol-Gel Derived Flexible Alumina Gel Monolith and the Intermediate Flexible Alumina Gel Monolith Produced Thereby
14. Shaped Sol-Gel Derived Ceramic-Ceramic Composites and Intermediate for Producing Same
15. Process for Obtaining an Intermediate Sol-Gel Derived Flexible Alumina Gel Monolith and the Intermediate Flexible Alumina Gel Monolith Produced Thereby
16. Novel Shaped Sol-Gel Derived Ceramic-Ceramic Composites and Intermediates for Producing Same

17. Method for Preparing Al_2O_3 Powder and Products

18. Method for Repairing or Joining of Ceramics and Products

19. Method for Fabrication of Homogeneous Sol-Gel-Derived Multi-Phase Materials and Gelling Control Agents Therefor

20. Method for Repair and Joining of Prefired or Fired Ceramics Using Sol-Gels

21. Method for Treating Sol-Gel Derived Composites

22. Electrodeposition of Ceramic Coatings Using Sol-Gel Processing and Compositions Thereof

23. Inorganic Salts as Peptizing Agents in the Preparation of Metal Oxide Sol-Gel Composites

24. Deposition of Ceramic Coatings Using Sol-Gel Processing with Application of a Thermal Gradient

25. Design of Lightweight Mirror Meeting Specific Surface Area, Density and Rigidity Requirements from Pure Silica Gels

26. Process of Molding Complex Structure from Pure Silica Gels Using Wax Molds

27. Method to Produce Light-Weight Mirror and Near-Net-Shape Mirror Through Mechanical Machining of Wet Pure Silica Gels

28. Method for Producing Large Silica Sol-Gel Oped Inorganic and Organic Compounds

29. Method for Production of Fast Radiation Hard Scintillating Sol-Gel Glass

30. Process of Molding Complex Structure from Pure Silica Gels Using Wax Molds