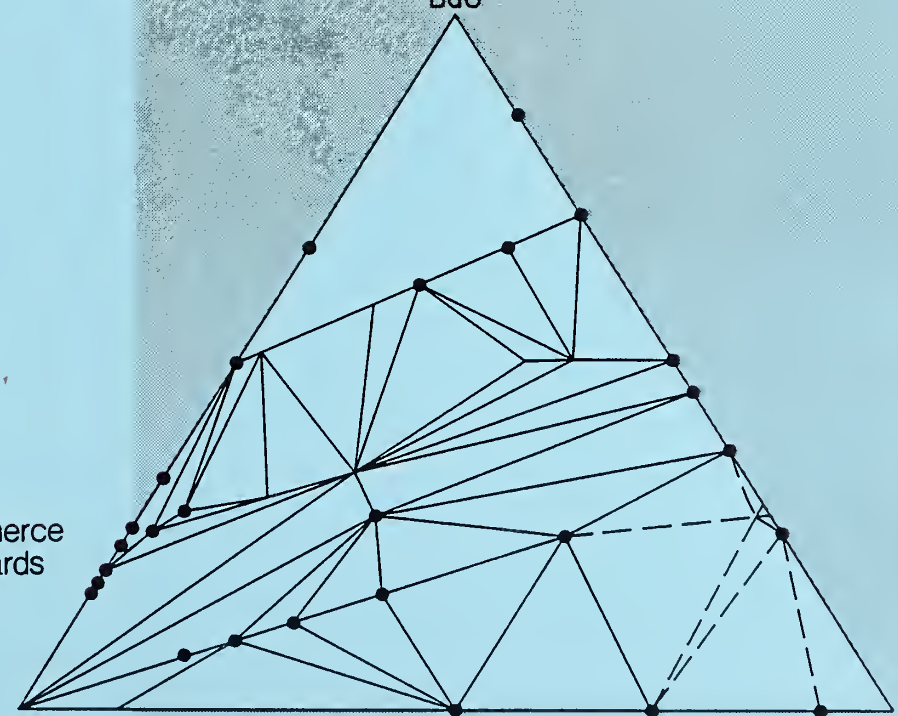
IMSE

Institute for Materials Science and Engineering

CERAMICS



NBSIR 86-3435
U.S. Department of Commerce
National Bureau of Standards

Technical Activities
1986

Cover Illustration:

The $BaO-TiO_2-Nb_2O_5$ Phase Diagram, determined by Dr. R. Roth, provides key data, for understanding and processing barium titanate dielectric ceramics. Further information can be found in the High Temperature Chemistry section of this report.

Courtesy of Dr. R. Roth, Phase Diagrams for Ceramists Data Center

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S.M. Hsu, Chief

January 1987

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INTRODUCTION

Introduction

The Ceramics Division was formally named in 1985 to reflect the increasing NBS emphasis on the science and technology base associated with advanced ceramics. The Division conducts research in many aspects of inorganic materials science and engineering. The primary technical focus of the Division is to develop basic understanding, novel measurement methods, standard reference materials, and standard reference data to enable industry to achieve key properties of ceramic materials through advanced processing.

As a result of the successful 1986 budget initiative in ceramics, the division has undergone considerable expansion in terms of personnel and research facilities. An extensive recruitment effort has resulted in the addition of 6 permanent staff, 14 post-doctoral research fellows and visiting professors. The graduate coop program was strengthened with the signing of agreements with Rutgers, Pennsylvania State, Drexel and, Northwestern Universities, and the University of Maryland. This brings the total number of graduate students in the division to nine. The addition of research personnel has been concentrated in the areas of ceramic processing and characterization. Considerable resources were also expended on equipment and facilities upgrading. A level 10 clean room was designed and is expected to be operational by the spring of 1987. Many new pieces of equipment and facilities are under construction or being purchased. These include a hot isostatic press, an automated x-ray diffraction system with high temperature (3000 °C) measurement capability, high temperature friction and wear measuring apparatus (1500 °C), a surface forces measurement instrument, an ultra-high mass spectrometer, and a laser Raman surface analyzer. This trend should continue in the 1987.

Programmatically, the division has been very active in both the domestic and international arena. Division staff participated heavily in many technical societies. Internationally, division staff lead the effort in International Energy Agency (IEA) coordinated multi-national cooperative research on powder characterization; and the VAMAS international collaboration on mechanical properties and wear of ceramics. The first NBS/BAM conference on ceramics was held in April 1986, at Berlin, to exchange technical information.

The Division's data programs received increasing attention and the programs were consolidated at the end of FY86 forming a new group. The group, Computerized Data Activities, centralized many emerging data activities with the ongoing successful activities in x-ray powder patterns and phase diagrams for ceramists.

Scientifically, there are many accomplishments in FY86. The most noteable are: the development of a diffuse reflective FTIR technique to determine the amount of beta phase in silicon nitride powder, the development of a new theory to explain increased fracture toughness with growing crack size; the measurement of internal strains in crystals using synchotron radiation; the preparation of Ba_3SmTiO_{27} single crystals leading to the discovery of a new dielectric material; formulation and solution of equations for the atomic structure of grain boundary interfaces in ionic ceramics using Green's function; and development of a novel synthesis route for SiC, TiB_2, and B_4C from precursors using alkoxide chemistry.

In FY86, the division addressed the needs of industry aggressively by visiting many companies and received industrial visitors. Many collaborative research efforts have been initiated. The division also participated actively in the establishment of a center for advanced materials at Pennsylvania State University sponsored by the Gas Research Institute. NBS will play a key role interacting with the center and its many industrial members to address some of the critical technical issues.

At the end of FY 86, we welcome the addition of the Synchrotron Analysis Group to our division. With the completion of the facilities at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, we look forward to the many exciting possibilities in exploring this new, powerful technique in addressing many materials science issues in advanced ceramics.

Stephen M. Hsu
Chief, Ceramics Division

September 1986

TECHNICAL ACTIVITIES

PROPERTIES/PERFORMANCE

MECHANICAL PROPERTIES

Sheldon Wiederhorn

Our program on mechanical properties has as its broad objectives: (1) the generation of new theories and data to elucidate fracture and deformation mechanisms in brittle materials; (2) the development of fracture methodology for studying the fundamental forces that exist between two near surfaces; (3) the investigation of ceramic microstructure and its relationship to mechanical behavior; (4) the understanding of the deformation and fracture properties that govern the mechanical response of ceramics at high temperatures.

Representative Accomplishments

- o A new theory to explain the observed rising fracture toughness of monophase ceramic materials with growing crack size was developed. The source of the toughness of ceramic materials is believed to originate in interlocking grains and unbroken ligaments that cross between the crack faces. These apply a closure force to the crack that must be overcome for fracture to proceed. This theory implies that the toughness of ceramic materials can be enhanced by microstructural design to increase the degree of interlocking of fracture surfaces. Studies have shown that this mechanism of toughening is applicable also at high temperature.

- o The role of surface forces in subcritical crack growth was explored for ceramic materials. Surface forces can account for a number of physical observations including the healing of ceramics when the external driving forces are removed, the change in slope of crack velocity curves when the external environments are changed, and the presence of fatigue limits. These predictions are being investigated through experimental studies on mica, glass, and sapphire.

- o A study of creep in tension has demonstrated the importance of cavitation to the creep process. Enhancement of the creep rate by cavitation results in stress distributions that are time dependent when components are subjected to bending stresses at elevated temperatures.

- o At equal creep strains, the creep rate of vitreous bonded ceramics appear to be insensitive to the volume fraction of glass in the material. By contrast the strain to failure is extremely sensitive to the volume fraction of glass, suggesting the small amounts of glass can lead to severe embrittlement at elevated temperatures.

Microstructure and Toughness

B.R. Lawn, C.J. Fairbanks, B.J. Hockey, and Y.-W. Mai[1]

[1] Guest Scientist, University of Sydney

During the past year the effect of contact damage on the strength behavior of a number of ceramic materials was studied. Specimens containing an indentation flaw at their centers were placed on a test fixture mounted on an inverted optical microscope. Loads applied to the specimens caused the cracks to grow. This growth was recorded on a video tape recorder so that the qualitative aspects of crack growth could be documented. Crack growth did not occur in a continuous fashion but in incremental steps. Fracture was often interrupted at one point only to restart at a second, adjacent point. These results suggest that interlocking grains and ligaments of unbroken material in the wake of the crack front serve to apply a closure force to the crack surface which must be overcome for the crack to propagate. Based on the above observations, a model of crack growth has been developed for predicting strength and failure time as a function of microstructure. The predictions are currently being tested in stress rupture studies at room temperature. The output of this project is expected to suggest changes in current methods of tailoring ceramic materials. A collaborative program with Dr. M.P. Harmer's ceramics processing group at Lehigh University is currently underway to explore this prospect.

Surface Forces

D.H. Roach, B.R. Lawn and S. Lathabai

In addition to the covalent and ionic cohesive forces that hold brittle materials together, there are weaker (but longer-ranged) adhesive forces which come into play when new surfaces are created, particularly in the presence of interactive environments: dispersion (van der Waals), electric double layer, solvation and cation-site forces are examples. These are the surface forces which are of such great importance in colloidal chemistry. We have shown in fracture experiments on mica, glass and sapphire that forces of this type are important also in strength properties of ceramics. They bear on the reversible nature of crack growth (i.e. crack healing), and hence on the existence of a "fatigue limit," i.e. an applied stress level below which propagation ceases. This interrelation between surface closure forces and crack properties is leading to a fundamentally new conception of fracture, whereby the underlying processes of bond rupture at the crack tip operate independently of the adhesive processes behind the tip. Scientifically, the decoupling of the two processes provides impetus for study on crack-tip structures at the atomic level. More importantly, it offers a potential new technique to measure surface forces using fracture.

High-Temperature Deformation and Fracture

S.M. Wiederhorn, T.-J. Chuang, N.J. Tighe, R.F. Krause, Jr., B.J. Hockey, L. Chuck, Y. Lu[1], J. Sun[2] and D.E. Roberts

[1]Guest Scientist, Shanghai Institute of Testing Technology, Shanghai, China
[2]Guest Scientist, Shanghai Institute of Ceramics, Shanghai, China

The development of new ceramics provides hope for high efficiency, enhanced performance of structural systems in high temperature, stress-bearing environments. However, before ceramics can be used in industrial applications, issues concerning reliability and service life remain to be resolved. With this in mind, our program on high-temperature properties of ceramics has five objectives: (i) the development of new theories that are capable of predicting time-dependent fracture and deformation behavior at specified loads and temperature; (ii) the development of new experimental techniques that can produce reliable creep data; (iii) the generation of a data base on commercially available ceramics and refractories; (iv) the investigation of kinetic processes that result in strength degradation and delayed failure; and (v) the examination of microstructures that promote understanding of mechanisms of response to creep and creep rupture.

High temperature fracture studies during the past year concentrated on magnesium chromate refractory, siliconized silicon carbide, and aluminum oxide. In all of these studies the strength or creep behavior was characterized as a function of temperature, time, and load.

In this project the creep rupture of magnesium chromate refractory has been quantified to correlate mechanical properties with failure mechanisms. Stress-rupture of as-received material was characterized as a function of temperature. Creep curves exhibiting work hardening strain could be fitted to a power law function of time, in which the exponents and coefficients were both stress-and temperature-dependent. The strain rate data were found to fit this empirical expression to better than 5 percent of the strain rate.

During the past year, the creep and stress-rupture behavior of siliconized-silicon carbide were characterized in four-point bending and pure tension as a function of temperature and stress. It was shown that cavitation nucleates early in the creep process from preexisting grain boundary defects. With additional deformation, the nucleation and growth of defects continues, eventually resulting in large cracks that lead to failure. Cavitation causes an enhancement of the creep rate and an increase in the stress exponent from 4, in the absence of cavitation, to 12 when cavitation occurs. As a consequence of the cavitation, the neutral strain axis for bending shifts towards the compressive surface of the test specimen. A method has been developed for locating the position of zero strain and is being used to collect data that can be compared with theoretical treatments of multi-axis creep.

The nucleation and growth of cracks at elevated temperatures was studied on commercial grades of vitreous bonded aluminum oxide by flexural loading. Vitreous bonded aluminum oxide was selected because it contained glass at the grain boundaries and could be used as a model for structural materials that are glass bonded. The creep-rate of vitreous bonded alumina oxide appears to be independent of the amount of glass initially present in the material, as indicated by the fact that experimentally idential creep rates were obtained for materials with ^{2}25 v/o and ^{2}8 v/o glass. This finding suggests a mechanism in which contact between aluminum oxide grains dominates the creep process. By contrast, the strain to failure (^{2}0.001 for the 8 v/o glass and ^{2}0.01 for the 25 v/o glass) appears to be sensitive to the volume fraction of glass. This, combined with data collected by transmission microscopy, suggests a strong dependence of crack nucleation and growth on the volume fraction of glass: the less glass the more sensitive the material is to crack growth. These data have practical implications with regard to load bearing capability to vitreous bonded materials.

GLASS AND COMPOSITES

Stephen W. Freiman

The Glass and Composite Group performs research in a number of areas, with a particular emphasis on the mechanical properties of glasses, polycrystalline ceramics, and ceramic matrix composites. There are major efforts being undertaken in the study of environmentally enhanced crack growth in brittle materials, e.g. gallium arsenide, on the effects of microstructure and chemistry on the fracture of polycrystalline ceramics such as those used in multilayer capacitors, and in the understanding of the fracture behavior of fiber-reinforced, ceramic-matrix composites. Data on the fracture behavior of brittle ceramics is needed in order to use these materials reliably in components which may be subject to mechanical or thermal stresses. Also, there is a considerable effort being placed in the development of non-destructive evaluation procedures for ceramics and ceramic matrix composites, with an emphasis on thermal wave analysis, In addition, there is ongoing work related to the development of glasses used as quantitative standards for elemental analysis. In all of these areas, the Glass and Composites Group is undertaking cooperative programs, both with personnel in other groups in the Ceramics Division, as well as with industrial and academic investigators in this country and abroad.

Representative Accomplishments:

- A new mechanism of fracture involving interface localized microfracturing was identified. This mechanism provides an explanation for the magnitude of the fracture toughness of a number of ceramic materials.

- Rates of crack growth in vitreous silica tested in basic solutions were shown to be greatly reduced by the addition of 1 mole of lithium to the solution. This observation has led to new ideas on ways to suppress stress corrosion in ceramics.

- The stress corrosion susceptibility of 94 percent alumina was shown to be directly related to the chemical composition of and the crystalline phases in the grain boundaries. This work has led to an improvement in our ability to choose materials having an optimum resistance to fracture.

- Fluorescent glass microspheres were developed as calibration standards for immunochemical analysis.

Fracture of Capacitor Materials

S. W. Freiman and T. L. Baker

Work has been performed to determine the effects of composition and microstructure on the fracture behavior of ceramics used in multilayer capacitors. Both the fracture toughness and the susceptibility to stress corrosion were shown to be strongly dependent on the chemistry and grain size of the particular material and were sensitive to the addition of minor quantities of constituents added to vary the electrical properties of the capacitor. An important observation was that the strength of the material at small flaw sizes could be correlated with its dielectric aging rate. This correlation is interpreted to be due to the fact that both strength and aging are controlled to a great extent by the magnitude of the internal stresses in the material.

Microstructure/Crack Interactions

P. L. Swanson[1]

[1]Post Doc

In-situ optical and scanning electron microscope observations of the subcritical fracture process have allowed us to evaluate several micromechanisms previously proposed as being responsible for a host of macroscopic fracture phenomena in aluminum oxide and glass ceramics. No evidence of distributed microcracking ahead of the fracture tip, generally regarded as a primary micromechanism of fracture, was found in any of the materials. Instead, interface-localized microfracturing was observed to operate at positions where tractions are transmitted across the nascent fracture surfaces. Interface tractions are provided by crack-surface interlocking and ligamentary bridging by "islands" of intact material left behind the advancing fracture front. The crack-length-and crack-opening-displacement-history dependence of this interface restraining-force provides a reasonable explanation for (1) the relatively high toughness of these materials (compared to individual constituents), (2) R-curve behavior (rising resistance to fracture with crack extension), and (3) the variability and test-geometry dependence of measured subcritical crack growth parameters.

Thermal Wave NDE

G. S. White, L. Inglehart[1], and E. LeGal LaSalle[2]

[1]Guest Scientist, Johns Hopkins University, Baltimore, MD.
[2]Guest Scientist, Ecole Superieure de Physique et de Chimie Industrielles, Paris, France.

Both mirage and photoacoustic thermal wave systems have been constructed and are operating. Thermal wave signals obtained on alumina specimens varying in porosity from 2 to 40 percent exhibited significant differences. Recently developed models are being applied in order to separate porosity effects from those due to surface roughness and optical absorption. The detectability of closed surface cracks in glasses and ceramics using thermal wave analysis is also being investigated.

Glass Standards

D. H. Blackburn and D. A. Kauffman

Work has progressed in the development of microspectrofluorimetric standards for instrument calibration in immunochemical analysis. Fluorescent glass microspheres 5 to 20 micrometers in diameter, containing U_3O_8, MnO, Tb_2O_3 and Eu_2O_3, have been produced and evaluated. Consideration is being given to issue these fluorescent spheres as SRM's.

TRIBOLOGY

Ronald Munro

Tribology is an interdisciplinary research activity concerned with the scientific aspects of the measurement and analysis of the friction and wear of materials and the control of those processes through lubrication. The applications of ceramic materials for which tribological factors are highly significant include low heat rejection engines, bearings, cutting tools, and a multitude of component parts for various engines and other mechanical apparatus. Neglect of tribological factors can have an immediate impact resulting in monetary costs, energy consumption, material losses, diminished production time, and reduced equipment efficiency. Improved understanding of tribological factors, therefore, may lead to a multifaceted savings for the national economy and may aid the position of U.S. industries vis a vis foreign competition. Such competition is being experienced most keenly in the developing applications of advanced ceramic materials. The tribological challenges encountered in the use of ceramics have motivated a technical program for the Tribology Group that encompasses three inter-related components. A prototypic tribological contact consists of two solid material bodies in relative motion interacting across an intervening lubricating medium in the presence of a local atmosphere. As a result of the interactions, the contact region may have relatively high temperatures and stresses. Thus, the material properties, wear mechanisms, and friction characteristics of the solid bodies form one important area of study. The variations of the chemical and physical properties of the lubricant form the second aspect of the program, while the interactions of the ceramic substrate and the lubricant form the third part. In all cases, the emphasis of the research effort is on understanding the mechanisms of the various processes.

Representative Accomplishments

- A new wear test method has been developed for the study of the friction and wear characteristics of ceramic materials. The new design was produced through a modification of the widely available four-ball wear tester to yield a ball on three flats configuration. The advantages of the new design include a greater flexibility in the source of ceramic specimens, easier sample preparation, and a sample geometry that is more amenable to pre- and post-test surface analysis.

- An important step was made towards the establishment of an international standardization of wear test methods through participation in the Versailles Project on Advanced Materials & Standards (VAMAS). Measurements on the series of materials in the round-robin testing included friction, wear, surface profilometry, and scanning electron microscopy of the prepared and worn surfaces.

- A new technique, incremental isothermal thermogravimetric analysis (I^2TGA), has been developed as part of a study of high temperature characteristics of lubricants for ceramic heat engine applications. The I^2TGA technique provides a rapid determination of evaporation rate as a function of temperature and the corresponding activation energy.

Such measurements are valuable in the assessment of lubricant volatility and are important to the control of oil consumption and volatility wear in ceramic heat engines.

- o Two standard reference materials (SRM) were issued and made available for purchase through the Office of Standard Reference Materials. SRM 1818 and SRM 1819 were developed as measurement reference materials that may aid the determination of small amounts of chlorine or sulfur in a lubricating base oil or similar material.

Wear Test Methods for Ceramic Materials

R. S. Gates, J. P. Yellets, D. S. Lim[1], F. Wang[2], O. Vingsbo[3], and R. G. Munro

[1]Guest Scientist, University of Illinois
[2]Guest Scientist, Tsinghua University
[3]IPA, Uppsala University

Ceramic materials are presenting a wide range of new and unusual challenges to the field of tribology. Underlying many of these challenges are the material properties of the ceramics, particularly the microstructure. Numerous results have shown that the performance of a ceramic material in a tribological context can vary dramatically from batch to batch of material production, even when customary and reasonable quality assurance practices are followed. Consequently, the need for wear test methodology that incorporates analyses of microstructural effects is quite apparent. This situation differs markedly from the more traditional wear testing of metals where batch to batch variations were minimal. One result of this difference is the immediate need for the design of wear test apparatus for which the test specimens may be readily subjected to pre- and post-test surface analysis techniques. Efforts to fulfill that need have been made during this fiscal year. Interests in the standardization of wear testing imposed further constraints on the design of the new apparatus. The availability of the apparatus and the configuration of the sample interfaces were also important. Such considerations led to a new design in the form of a modification of the widely available four-ball wear tester. By redesigning the sample chamber such that the three stationary balls were replaced by three flats, a ball on three flats configuration was produced. The new design meets the primary technical requirements for ceramic wear testing while providing a technique that will be widely available at relatively low cost. Tests on measurement repeatability have shown that both friction and wear determinations were repeatable within five percent.

Lubrication of Ceramic Materials

P. Pei, C. S. Ku, K. L. Jewett, L. S. Hsu, D. E. Deckman, R. S. Gates, and R. G. Munro

The control of wear in ceramic devices such as heat engines requires the use of a lubricant capable of sustained operation at high temperature. The minimum requirement for a short-term near-future lubricant is operation at intermediate temperatures to 400 °C. Current automotive lubricants have limiting peak temperatures of about 250 °C for short duration. The principal concerns for high temperature lubricant operation are oxidation, thermal degradation, volatility wear, and chemical corrosion. These processes are directly related to lubricant effectiveness, lubricating film formation, sludge or harmful deposits, and oil consumption. Under in-service conditions, lubricants evolve through a complex series of molecular structural changes resulting from heating and chemical reactions. The net effect of the process is a degradation of the lubricant effectiveness, i.e., a reduction in the ability of the lubricant to afford protection to the tribological surfaces undergoing wear. This degradation process is strongly dependent on the temperature and is accelerated by elevated temperatures. The changes in molecular structural composition may be considered as the results of two types of processes: thermal, such as depolymerization, and chemical reactions, such as oxidation. The thermal stability of a lubricant is the intrinsic capacity of the lubricant to resist molecular structural changes under heating in the absence of oxidation. Oxidation reactions in lubricants tend to accelerate viscosity increases, corrosion, wear, and the production of sludge-forming deposits. Hence, both thermal and oxidative stabilities are principal aspects of advanced lubrication concepts. Efforts to develop suitable measurement capabilities have led previously to several complementary techniques including a novel temperature scanning thermogravimetric analysis (TGA) procedure, differential scanning calorimetry, micro-oxidation testing, and oxygen uptake tests. A new technique, an incrementally isothermal TGA procedure, has been developed to study the volatility characteristics of candidate high temperature lubricants. The new measurement technique provides a rapid determination of evaporation as a function of temperature and the corresponding energy of activation. Results from the new technique will provide key data to be used in conjunction with thermal, oxidative, and wear test results to develop and understand high temperature lubrication concepts and ceramic-lubricant interactions.

Standard Reference Materials

P. Pei, C. S. Ku, L. S. Hsu, K. L. Jewett, and R. G. Munro

Standard reference materials (SRM) are a vital part of measurement technology and are often crucial to the calibration of industrial instruments or for the quantitative interpretation of analytical data. The development of a series of such SRMs for use with automotive lubricants has been undertaken as part of an ongoing effort to improve analytical procedures for lubricant analysis. A goal of the project is to produce three calibration standards that will enable quantitative measurement of three important elements that frequently occur in relatively low concentrations: chlorine, sulfur, and nitrogen. Two of these standards, SRM 1818 (chlorine) and SRM 1819 (sulfur) were released for sale during this fiscal year. Work is continuing towards a standard for nitrogen in base oils. Other work on reference materials included the production of a new batch of SRM 1817, a fuel and metal catalyst package for oxidation testing of automotive lubricants. The stock of the original 1000 units issued in 1983 was depleted in early 1986 because sales of the SRM were relatively rapid as a result of world-wide use of the NBS developed thin film oxygen uptake test. Certification testing of the new batch of SRM 1817 is in progress.

OPTICAL MATERIALS

Albert Feldman

The objective of the optical materials group is to provide data, measurement methods, standards and reference materials, concepts, evaluated data, and other technical information on the fundamental aspects of processing, structure, properties and performance of optical materials for industry, government agencies, universities, and other scientific organizations. The program supports generic technologies in crystalline, glassy, and thin film inorganic optical materials in order to foster their safe, efficient and economical use. Research in the group addresses the science base underlying new advanced optical materials technologies together with associated measurement methodology.

Two principal areas of optical materials research are being covered:

> Thin optical films addresses structure/processing relationships and how they affect properties and performance as related to optical coatings and integrated optics.
>
> Materials for optical signal processing addresses structure/processing relationships of crystalline electro-optical materials important as modulator and optical memory materials.

In addition to the principal areas of activity, the group maintains the capability to measure refractive index, thermo-optic constants and piezo-optic constants of optical materials.

Representative Accomplishments

- Transmission electron microscopy (TEM) and x-ray diffraction (XRD) studies of electron-beam evaporated zirconia optical films show that the film microstructure is in the form of conical columns. These results explain both the change of crystal structure with distance from the substrate and the refractive index inhomogeneity of zirconia films. Mixed zirconia-silica films observed to be amorphous by x-ray diffraction have been shown to be amorphous by electron diffraction as well.

- Apparatus that uses photo-thermal radiometry (PTR) to measure the thermal properties and adhesion of thin films has been constructed. Delamination of films from substrates is clearly observed when a suitable shear stress is applied to the thin film-substrate specimen. Measured thermal diffusivities agree well with values in the literature.

- Synchrotron topography at the National Synchrotron Light Source (NSLS) of Czochralski-grown bismuth silicon oxide (BSO) has shown elaborate arrays of defects associated with growth irregularities. The detailed understanding gained in collaboration with crystal growers should lead to greatly improved optically active materials.

Thin Optical Films

A. Feldman, E. N. Farabaugh, Sun Yining[1], H. H. Chen[2], R. Gomez Barengo[3]

[1]Guest Scientist, Lanzou Institute of Physics, Peoples Republic of China
[2]Guest Scientist, Precision Instrument Development Center, Taiwan
[3]Guest Scientist, Instituto Politecnico Nacional. Mexico

The microstructures of thin films of ZrO_2 and ZrO_2-SiO_2 formed by electron-beam coevaporation have been examined by x-ray diffraction and transmission electron microscopy (TEM). The films, which ranged in thickness from 10 nm to 150 nm, were grown on mica substrates coated with carbon. The substrate temperature was 325°C. For the TEM studies, the specimens were placed in water which caused the films to separate from the mica substrates. The films were allowed to settle on copper grids. Results of the TEM examinations suggest that films composed of 100% ZrO_2 grow by the formation of conical polycrystalline columns. Near the substrate the columns are of small diameter and contain a single crystalline phase, but at increasing distances from the substrate the column diameters increase and material with two crystalline phases occurs. Electron diffraction suggests that an amorphous phase is also present adjacent to the substrate. Small additions of SiO_2 to the film composition result in a smaller column diameter at a given distance from the substrate. Films with greater than 30% SiO_2 by volume, which display an amorphous x-ray diffraction pattern, have been shown to display an amorphous electron diffraction pattern as well. The surfaces of the amorphous films are nearly featureless and are significantly smoother than the surfaces of 100% ZrO_2 films. This work will assist in the development of optical films with greater optical and mechanical stability.

Materials for Optical Signal Processing

B. Steiner

Monochromatic topographs of several slices of a single high quality bismuth silicon oxide boule show complex strain patterns indicating previously unsuspected irregularities in Czochralski growth nominally under effective control. These features can be compared to provide a detailed understanding of their development. For example, the prominent strain on the right edge of the fringed central square in Figure A, a Bragg topograph from the NBS beamline at NSLS, is shown in Figure B, a corresponding Laue topograph also from the NBS line, to be due to the temporary cessation of growth in the peripheral region on the right. The central area, growing in the [001] direction, and the three other peripheral regions growing in the [011] direction meanwhile continued to grow in step with each other in the [001] direction. Three successive, dark [011] planes toward the top of Figure B can be observed to intersect the halted [011] plane on the right in the form of characteristic angles formed by the critical interface and the bottom edge of the slice. From such detailed studies, in which the Laue geometry permitted by the intensity of the synchrotron is crucial, crystal growth by many differnt techniques is expected to yield optically active materials of greatly improved quality.

Photo-thermal Radiometry for Measuring Thermal Properties and Adhesion of Thin Films

H. P. R. Frederikse and A. Feldman

A principal goal of this project is to put the measurement of the adhesion between a film and a substrate on a more quantitative basis. We want to measure the adhesion of coatings as a function of surface condition, substrate temperature and deposition technique. The system under investigation is a dielectric film (1-100 μm thick) on a metal substrate. Delamination is brought about by stressing the sample in a calibrated bending device. For detecting the onset of delamination we use a thermal wave technique known as photo-thermal radiometry (PTR). This method uses a chopped laser beam to produce a modulated temperature at the surface of the film. The heated spot on the specimen is focussed onto an InSb infrared detector which monitors the amplitude and phase of the temperature at the specimen surface. The phase of the signal is sensitive to inhomogeneities in the specimen, like voids at the interface. By translating the specimen across the beam one can map variations at the film-substrate boundary. We have performed a series of scans of specimens under increasing flexural loading and have observed the initiation of film break-up or delamination. Films currently being investigated are plasma sprayed chrominum-oxide and magnesium zirconate on aluminum (~ 50 μm thick).

Another goal of this project is to measure the thermal diffusivity of thin films. This measurement is important in the case of films subjected to thermal loading such as optical films in high power laser beams. This property can be correlated with the density (porosity) of films. In the case of films of mixed composition, the measurements can be correlated with models for the thermal behavior of mixed films. In this case, the method of measurement requires measuring the thermal signal as a function of chopping frequency which varies the diffusion length, and, hence, the probing depth of the thermal wave. Trial measurements of thermal diffusivities indicate good agreement with the literature.

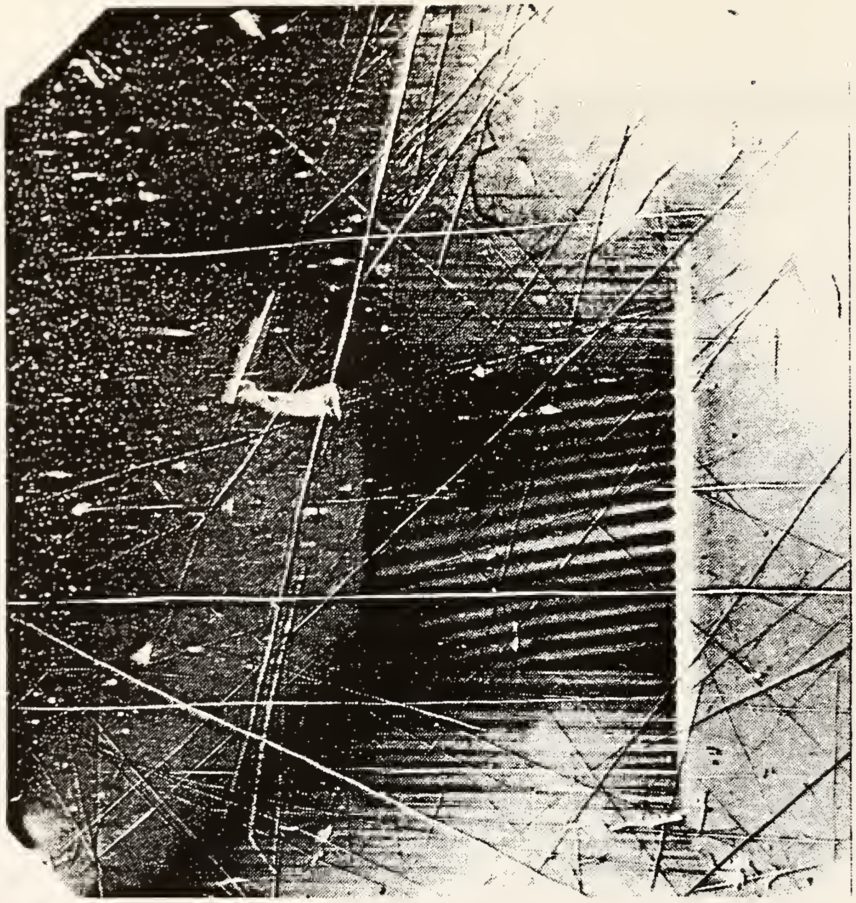


Figure 1A. Bragg topograph of bismuth silicon oxide crystal.

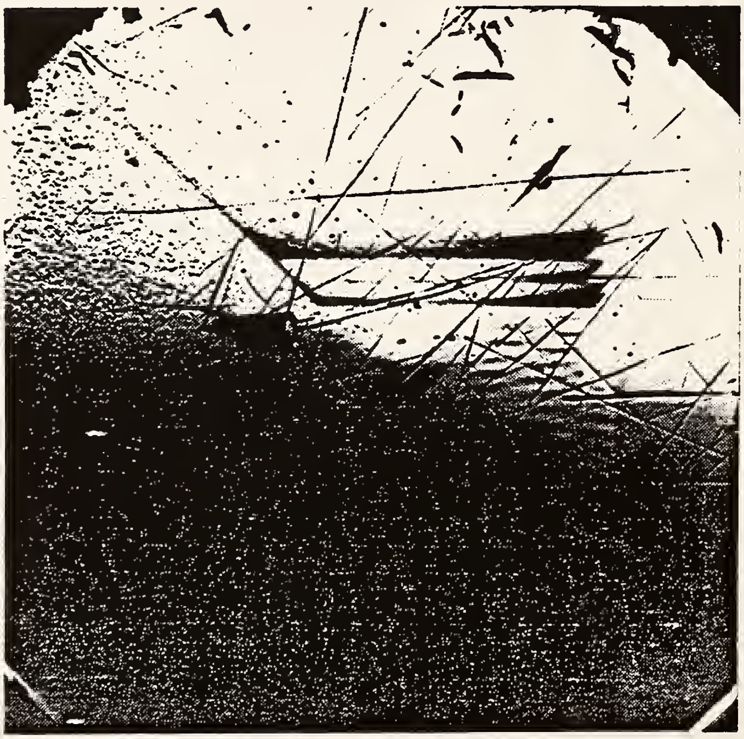


Figure 1B. Laue topograph of crystal shown in Figure A.

STRUCTURE/STABILITY

HIGH TEMPERATURE CHEMISTRY

John Hastie

Our program in high temperature chemistry and phase equilibria emphasizes the structural, thermodynamic, and chemical-kinetic behavior of materials in high-temperature/high-pressure (gaseous) process and service environments. Solid-liquid-vapor phase equilibria, crystal and molecular structure, and reaction mechanisms of ceramic, glass, slag, salt and other inorganic systems are determined experimentally and through modeling. The Phase Diagrams for Ceramists Data Center compiles and critically evaluates ceramic phase diagrams in cooperation with the American Ceramic Society.

This activity serves new technologies, such as those based on processing of advanced ceramics, refractory ceramic durability, nuclear waste management, electronic ceramics, and more efficient fossil fuel combustion. Industry and other government agencies use the results (a) for performance predictions and test method development in new high technology applications, and (b) to support materials processing at high temperatures.

The research addresses: development of new or improved experimental methods, their application to determination of basic data and new concepts, modeling of ceramic/metal gas-liquid-solid equilibria, and computer-aided critical evaluation and compilation of ceramic phase equilibrium diagrams. Molecular-specific experimental methodologies and theoretical modeling tools are also being developed and applied to the determination of basic thermochemical and kinetic data and chemical reaction mechanisms. In support of phase diagram determinations, and for the completion of thermodynamic cycles, the characterization of condensed phase composition and structure is achieved by x-ray or neutron diffraction, scanning and transmission electron microscopy, and electron spectroscopy for chemical analysis (ESCA).

During the past year, the research has focussed on six interrelated subtasks: (1) Phase Diagrams for Ceramists Data Center; (2) Phase Equilibria and Structural Chemistry; (3) High Temperature Chemistry; (4) Data Center on Materials and Components for Fossil Energy Applications; (5) High Temperature Thermophysical Properties; and (6) Steel Slag-Refractory Thermochemistry, a new initiative. The following discussion highlights some of these areas.

Representative Accomplishments:

- The National Bureau of Standards (NBS)-American Ceramic Society (ACerS) program for a ceramic phase diagram data center, completed the first full year of its expansion plan. Novel procedures were developed and implemented for computer storage and retrieval of bibliographic files, ternary diagram digitization, computer editing, topographical manipulation, and for preparation of production-quality ceramic phase diagrams. A bibliographic data bank for oxide and salt-containing phase diagram literature was completed and a hard-copy volume published. A graphics data bank containing about 2000 binary and ternary phase diagrams was also developed.

- A book on "Construction Materials for Coal Conversion--Performance and Properties Data" was published. This activity represents an evaluated compilation of data provided by the Department of Energy materials research contractor's reports. The book completes the series covering alloy and ceramic materials.

- A predictive oxide phase equilibria model, developed earlier, was refined for steel making applications and modified for use by non-experts. The computer-based model was transferred to several industries involved with steel production and coal conversion (magneto-hydrodynamic, fluidized bed combustion) for use in process design.

- Basic vaporization data and processing mechanisms were determined for simulated nuclear waste under high temperature processing conditions. This work was supported by the Dupont Atomic Energy Division, Savannah River Laboratory, to provide key vaporization-loss data for the waste vitrification process being developed by Dupont. The significant cesium vapor transport found was particularly enhanced by the presence of the process impurities carbon, halogen, and water vapor.

- The first direct measurement of the enthalpy of melting for tungsten was determined using a unique levitation calorimetric technique. The result should serve as a benchmark for testing new phase transition theories, including melting. The work, performed collaboratively between NBS, General Electric, and Rice University, also demonstrated proof-of-concept for levitation of molten materials in space. A prototype apparatus for space flight experiments was also developed.

- The preparation of single crystal compounds in the Ba-Sm-Ti-oxide system, together with their structural determination, has led to industrial development of a new ceramic dielectric. The dielectric, based on $Ba_3SmTi_9O_{27}$, has a very low dielectric loss, essentially zero temperature coefficient in the dielectric constant, and about twice the dielectric constant of any microwave ceramic filter device currently on the market. This development resulted from a collaboration between NBS, industry and various national and international university groups.

Phase Diagrams for Ceramists Data Center

J. W. Hastie, H. M. Ondik, R. S. Roth, L. P. Cook, M. A. Clevinger, M. Lukens, P. K. Schenck, H. Parker[1], P. Davidson[4]
J. Dennis[2], T. Brittle[2], S. Cauley[3], R. Yan[3], M. Pryor[3], M. Rodtang[3], P. O'Neil[3], K. Davis[3], and C. Messina[2]

[1]Guest Scientist, NBS, American Ceramic Society.
[2]Research Associate, American Ceramic Society
[3]Student Research Associates, American Ceramic Society
[4]NRC Post Doc

NBS has a well-established joint data activity with the ACerS and is closely coupled with current needs, as identified by NBS and ACerS advisory committees. Recent research activity in this area has been expanded in response to the increased complexity and quantity of new phase diagrams, together with an expanded dependence by industry and others on critically evaluated diagrams and related thermodynamic data, and include the following tasks:

(a) Evaluation/Production. Considerable progress has been made in the preparation of new "Phase Diagrams for Ceramists" volumes for oxides, oxygen-containing systems, sulfides and halides. About 6800 phase diagrams are being evaluated for these volumes and an anticipated NBS completion date for the next volume is December 1986. Literature search and reference recovery is also in progress to include new systems containing Periodic Table Groups IVA, VA, and VIA elements (including many semiconductor compounds) and also boride, nitride, and carbide compounds.

(b) Data Base Development. Progress has continued both in software development and in file building for the bibliographic and graphics data files. The bibliographic file software, developed in collaboration with the NBS Office of Standard Reference Data, has been expanded and revised. The software provides not only for the preparation of fully transportable data files (all ASCII characters) of totally variable length but also for the generation of files to feed other data bases and any rapid-search data base management system. The software also provides methods for easy updating, editing and rearranging of the data elements. The graphics input and editing software has been expanded so that ternary diagrams are being digitized routinely. The utility of the ternary phase equilibria data is being greatly enhanced through development of a general purpose rotate and section program for three dimensional (3D) ternary diagrams. Figure 2 shows a representative example of one of the many views possible for a 3D phase diagram constructed from the planar-projection ternary and binary diagrams. About 1000 binary and ternary diagrams have been digitized, edited and filed in a computer data bank.

(c) Modeling/Optimization. Current activities focus on: (1) the development of new solution models for phase diagram optimization and prediction (2) incorporation and testing of NBS-developed solution models, and others, into existing computer codes for phase diagram optimization, (e.g.; with K. Spear, Penn State), (3) application of the THERMFACT computer code, with its extended regular solution model, to phase diagram optimization for relatively simple molten salt systems, (4) development of a thermodynamic data base for complex oxide systems, for use with the SOLGASMIX (Ericksson, Sweden) and other computer codes applicable to phase equilibria predictive modeling, and (5) development of solid-solution models for complex oxide systems. Progress in each of these areas has been documented elsewhere in reports, archival publications, and through invited talks.

Phase Equilibria and Structural Chemistry

R. S. Roth, L. P. Cook, E. R. Plante, K. Davis[1], R. J. Cava[2], H. Parker[3], P. K. Davies[4], L. Ettlinger[5]

[1]Student
[2]Guest Scientist, AT&T Bell Laboratories
[3]Guest Scientist, NBS, American Ceramic Society
[4]Guest Scientist, University of Pennsylvania, Philadelphia, PA
[5]Research Associate, JCPDS

Experimental research, performed as indirect support of the Data Center program, and for Other Agency projects, includes both classical determination of phase diagrams (i.e., direct phase identification) and indirect measurement based on Gibbs energy relationships. In the latter case, use is made of vapor pressure measurement using unique NBS facilities developed under the High Temperature Chemistry program. The classical phase equilibria program currently emphasises oxide systems important to advanced ceramic technology. One example is shown in Figure 3 for the very complex system $BaO-TiO_2-Nb_2O_5$. This system is very important for the understanding and development of microwave dielectric ceramics with high dielectric constants and low dielectric loss and temperature coefficients.

(a) Stored Chemical Energy Systems (SCEPS): The $Li_2O-Al_2O_3$ system. During the past year, work was performed in response to basic data needs of the Office of Naval Research (ONR) and Garrett Corporation for development of stored chemical energy propulsion systems. The system of interest is based on the exothermic reaction of a Li/Al alloy with steam to yield $Li_2O-Al_2O_3$ phases and hydrogen, which is to be burned for additional thermal energy. Also, the join $LiAlO_2-Al_2O_3$ is of particular interest to the aluminum industry for production of ceramic crucibles used in the processing of lithium-aluminum alloys for aerospace application.

(b) Thermogravimetric Study of SCEPS Oxidation Reactions. In addition to the detailed work on $Li_2O-Al_2O_3$ discussed above, exploratory studies of eight alternative stored chemical energy systems have been conducted. The aim of these studies was primarily to determine the reaction kinetics and products. The reaction products involve complex phase relations among mixtures of salts, metals and oxides. The eight fuel/oxidant reaction schemes of interest are: Li/H_2O; H_2/O_2 [1], Li/H_2O; NaO_2/H_2O; H_2/O_2 [2], $MgAl/H_2O$; H_2/O_2 [3], $LiAl/ClO_3F$ [4], $LiAlMg/ClO_3F$ [5], $LiBe/ClO_3F$ [6], $Li/C_{11}F_{20}$ [7], and LiB/NF_3 [8].

(c) Ceramic Dielectric Barium Polytitanate Systems. A small amount of Nb_2O_5 is often added for commercial preparation of $BaTiO_3$ ceramics in order to optimize the dielectric properties. Electron diffraction has shown that a second phase exists in the grain boundaries which is not the polytitanate $Ba_6Ti_{17}O_{40}$ (6:17 oxide mole ratio) known to be in equilibrium with $BaTiO_3$ in the binary system. Investigation of the ternary $BaO-TiO_2-Nb_2O_5$ has shown that at least four new phases exist in this system with less than 5 mol percent Nb_2O_5. They have been tentatively identified from single crystals as $Ba_6Ti_{14}Nb_2O_{39}$ (8-layer orthorhombic), $Ba_{14}Ti_{40}Nb_2O_{99}$ (20-L orth), $Ba_{10}Ti_{28}Nb_2O_{12}$ (7-L monoclinic) and $Ba_{18}Ti_{54}Nb_2O_{132}$ (13-L mon). Investiga-tions in the ternary systems $BaO-TiO_2-SnO_2$ and $BaO-TiO_2-ZrO_2$ have proven the existence of the compound $Ba_2Ti_5O_{12}$. This phase is apparently only stable under high temperature when ZrO_2 is incorporated in the lattice. The true composition is thus $Ba_2T_{15-x}Zr_xO_{12}$. The unit cell dimensions and crystallographic symmetry were characterized from single crystals.

High Temperature Chemistry

J. W. Hastie, E. R. Plante, D. W. Bonnell, P. K. Schenck, A. B. Sessoms, M. Wilke

This activity develops and applies new or improved measurement techniques for the molecular-level analysis of high temperature vaporization and condensation processes. The processes occur over ceramic solids and melts, coal slags, glasses, and salts and in process atmospheres containing reducing, oxidizing, carbonated, halogenated, sulfated, hydrous, and other reactive components. These environments are characterized by extremes of temperature (typically 10 - 5000 K), gas pressure (10^{-6} - 10^{2} atm), chemical reactivity, and phase complexity. The conditions and data obtained are generic to high temperature ceramic processing environments, and in applications where hot corrosion and high temperature oxidation are materials-limiting factors. Representative activities are as follows:

(a) Nuclear Waste Glass Processing. Industrial and DOE plans for nuclear waste storage require the waste to be incorporated into a borosilicate glass. Vapor pressure data are needed for these glass-waste forms in order to optimize the process conditions (e.g., temperature, composition) and minimize the loss of radionuclides by vapor transport during the high temperature processing of the wastes. In earlier NBS work the vaporization losses of radionuclides was determined for the final process glass at temperatures around 1100°C. Recent studies have dealt with the pre-glass forming stage at temperatures between 200-1000°C. Using Kundsen effusion and transpiration mass spectrometry, significant transport of Cs was found and its mechanistic relationship to the presence of H_2O, halogen, and carbon process-impurities established.

(b) Laser-Induced Vaporization Mass Spectrometry. Degradation of materials by high powered lasers is important in, for example, the design of laser fusion processes, laser welding, laser processing of ceramics, laser etching of semiconductor components, and in the durability of refractories in defense and space applications. In addition, the use of lasers as point heat-sources has the potential for characterizing materials phase transformations at very high temperatures and under essentially containerless conditions. We have undertaken fundamental studies of laser-induced molecular level vaporization with initial emphasis on graphite, boron nitride and other refractory materials.

(c) Ultra-High Molecular Weight Mass Spectrometry -- Application to The Cluster State of Matter. The unique capabilities of the high temperature mass spectrometry laboratory are being extended to include the very high molecular weight (up to 20,000 amu) cluster intermediate species present as condensation nucleii in supersaturated vapors. A reflectron time-of-flight (TOF) mass spectrometer has been designed for this application and construction is progress.

(d) Steel Slag-Refractory Thermochemistry. During the past year, a new project was begun as part of the NBS Steel Research Program. This work represents an extension of our earlier modeling work which focussed on MHD slags. The objective is to develop a generally applicable computer-based model of slag-refractory thermochemical interactions. To-date an experimentally validated multicomponent equilibrium model has been developed for any solid or liquid-containing mixture of Na_2O, K_2O, CaO, MgO, FeO, Fe_2O_3, Fe_3O_4, Al_2O_3, and SiO_2.

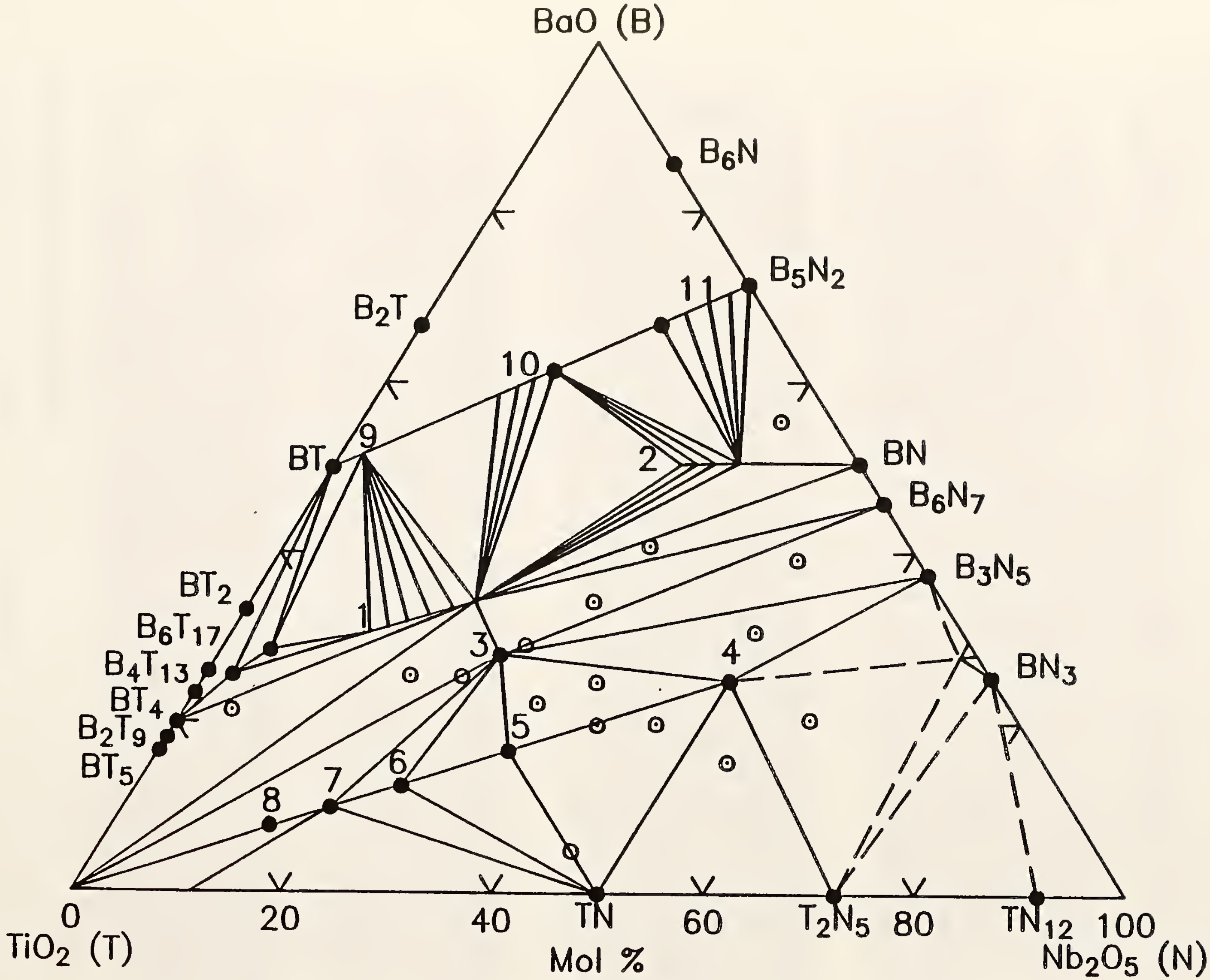


Figure 3. Phase diagram of the system $BaO-TiO_2-Nb_2O_5$.
BT_9N_2 - $BaTi_9Nb_4O_{29}$, BN - $BaNb_2O_6$ etc...

1	$B_3T_4N_2$ ss	4	BTN_2	7	BT_7N_2	10	$B_8T_3N_2$ ss
2	$B_6T_2N_4$ ss	5	BT_3N_2	8	BT_9N_2	11	$(B_6TN_2-B_5N_2)$ss
3	"$B_3T_5N_3$"	6	BT_5N_2	9	BT ss		

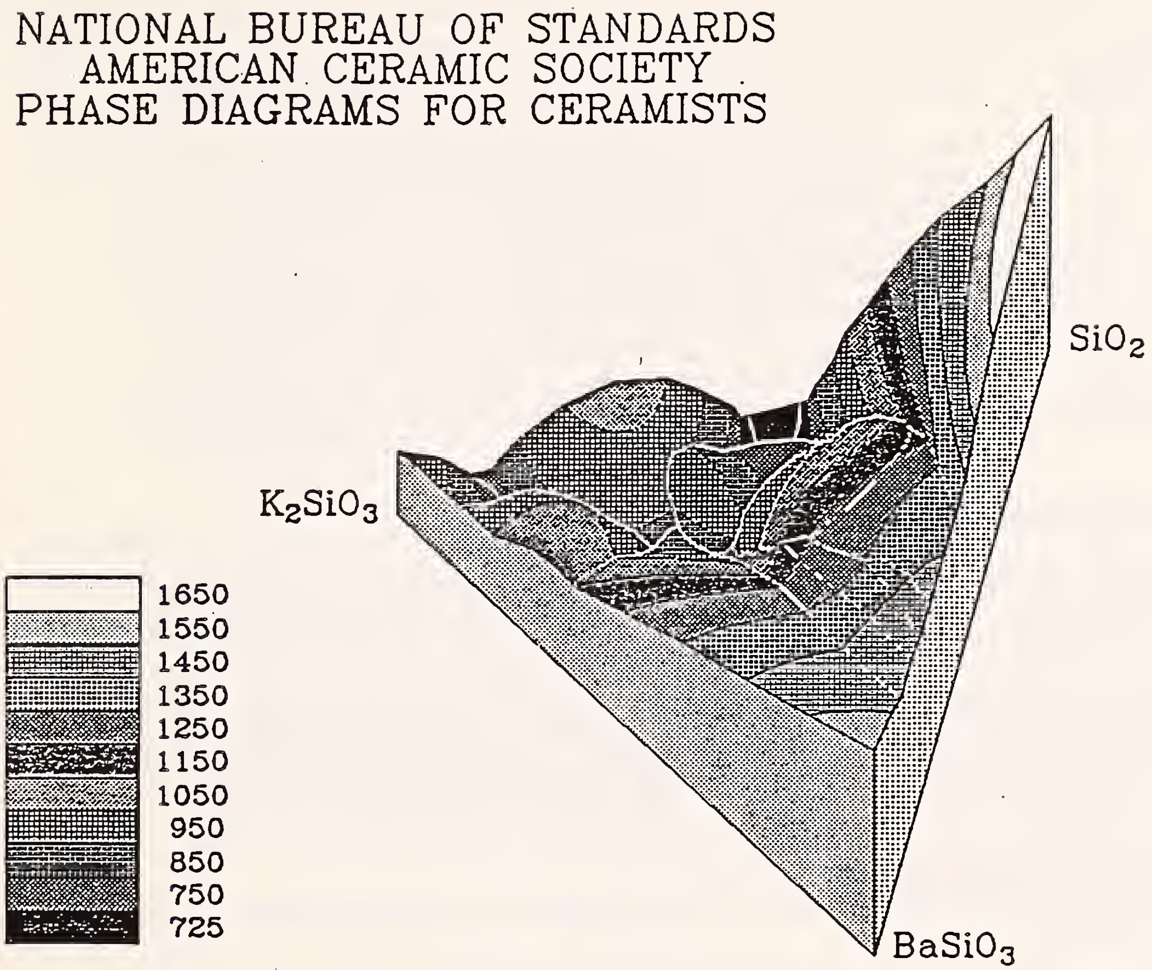


Figure 2. Computer constructed three-dimensional phase diagram representation, based on the planar-projection ternary and binary diagram data.

STRUCTURAL CHEMISTRY **Stanley Block**

Knowledge of effects of high pressure and temperature on the structure, phase relations, and physical, mechanical and chemical properties of materials is necessary for their efficient industrial utilization. Such information is essential for improving our understanding of the parameters that are critical to ceramic processing and transformation toughening in order to produce more fracture resistant ceramic products. The stability and retention of high pressure phases as toughening agents to improve the properties of materials, particularly ceramics is a new area that requires attention. To carry out these investigations effectively, we must also improve our measurement and standards capability at high pressures.

Representative Accomplishments

- o The critical variables to retain potential transformation toughening high pressure phases were determined using the high pressure form of zirconia as a model material.

- o Comparative sintering studies of pure and doped zirconia showed that the toughness of zirconia compacts sintered at high pressure is due to the high pressure phase serving as a new toughening agent and not pressure sintering.

Pressure Transformation Toughening

S. Block, G. Piermarini

The question of whether the improved toughness of zirconia samples sintered at high pressure and temperatures below 500°C was due to pressure sintering or transformation toughening was solved by comparing yttria doped zirconia, which has no high pressure form, with pure zirconia. Fig. 4 illustrates the indentation patterns for the pure and doped materials under identical conditions, 8.6 GPa and 250°C for 1.5 hours. Although of only slightly greater hardness (10.3 GPa for the pure versus 8.9 GPa for the doped zirconia), the pure material is much tougher than its doped counterpart, as evidenced by the distinct lack of radial cracking at the impression corners. This superior toughness is attributable to the presence of the high pressure metastable phase and not pressure sintering. The above study (carried out in collaboration with B. Hockey and B. Lawn of the Mechanical Properties Group) opens up the prospect of using high pressure methodology as an investigative tool in the search for new transformation toughening agents in ceramics.

Investigations to determine the mechanisms involved in retaining the high pressure phase of zirconia were conducted. Pressure was used for the driving force for the transformation, while temperature was used solely as a means of modifying the extent of the defect population participating in the nucleation of the transformation. Samples of particle size of about 0.03 μm (sample 1) and larger 0.1 μm (sample 2) were treated by the routes shown in Fig. 5. Different processing of zirconia powders resulted in retention of different amounts of the high pressure phase. In (a) the retention was 40% for sample 1 and zero for sample 2. For (b) retention was 100% for sample 1 and 50% for sample 2. For (c) the retention was 20% for sample 1. The dashed lines indicate the boundary between the high and low pressure phases for forward and reverse transformations.

We can draw the following conclusions from the experiments:

(1) Thermal treatment, hydrostatic environment, and particle size are all factors which influence the retention of the metastable high pressure phase.

(2) The results support the idea that the transformation is initiated at nucleation centers whose potency can be minimized by thermal treatments.

The other aspect of this program is the search for new transformation toughening agents. Crystal chemical principles can roughly guide the search and once a candidate material has been found can suggest substitutions to reduce the transition pressure. The transition pressure of several compounds were determined. Some were promising and suitable analogues and solid solution series were prepared by L. Cooke, R. Roth and K. Davis of the High Temperature Chemistry Group. As anticipated, the transition pressure was inversely related to ionic size. Potential toughening agents which transform in the 0.5 to 1.5 GPa range, significantly lower than for zirconia, were found. Currently studies are underway to evaluate their toughening ability.

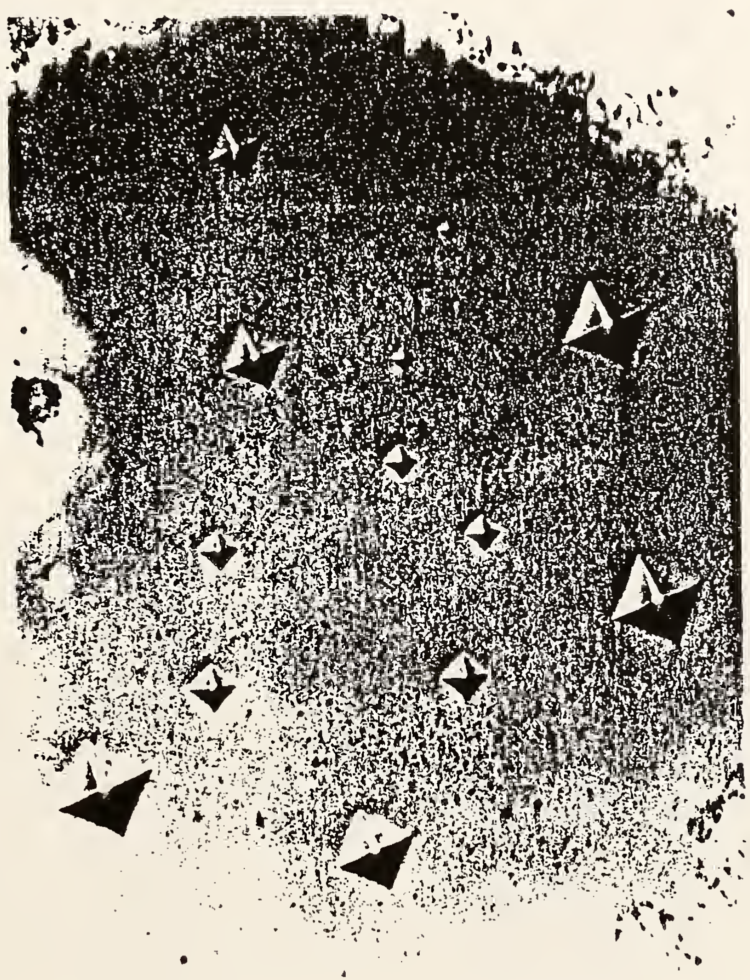
Kinetics of Decomposition of High Energy Materials as a Function of Pressure

G. Piermarini, S. Block and P. Miller[1]

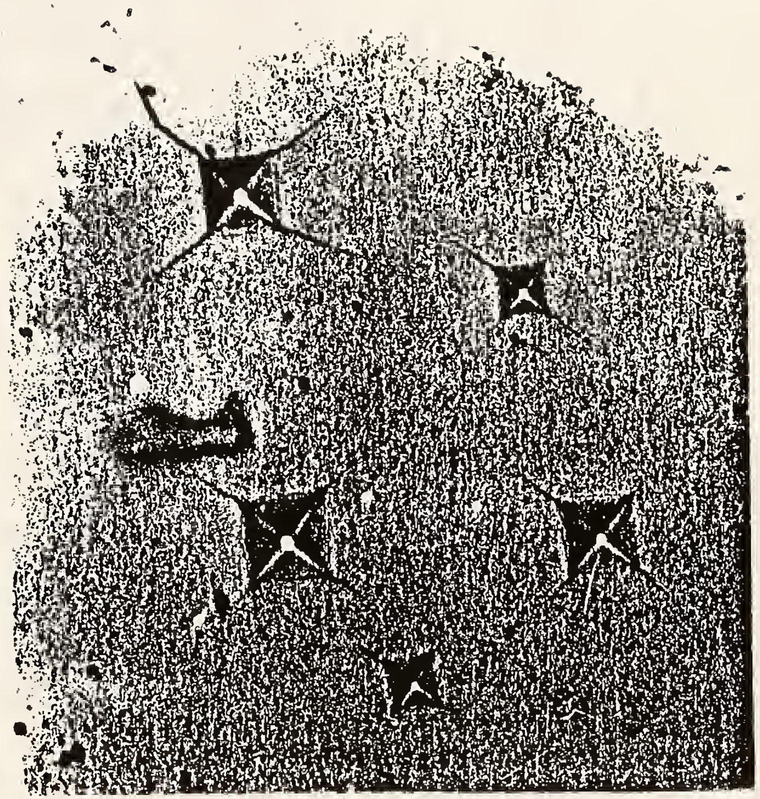
[1]Naval Surface Weapons Center, White Oak, MD

This project, which is funded by the Army Research Office, is designed to provide information on the parameters that affect the kinetics of thermal decomposition of high energy materials. The study of the phase behavior, melting point and decomposition of HMX as a function of pressure and temperature were carried out. The results are in the process of being published.

Fig. 4 Indentations on Compacts Prepared at P=8.66GPa, T=250°C, t=1.5 hrs.



ZrO_2



$ZrO_2 \cdot 12w\%Y_2O$

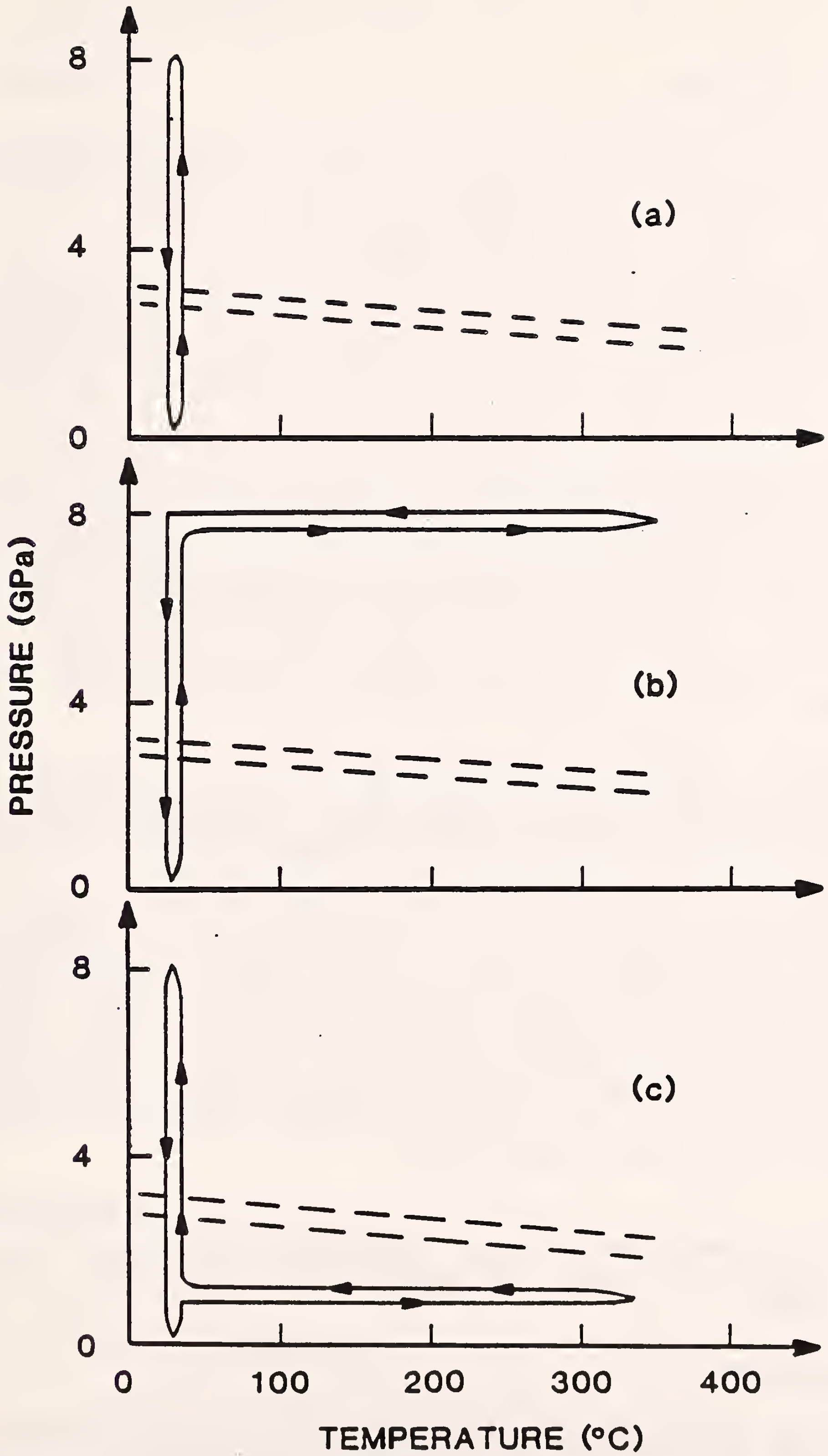


Fig 5 Effect of processing route on retention of high pressure ZrO_2 phases.

Ceramic Powder Characterization

Alan Dragoo

Improved characterization of ceramic powders is recognized as one of the key factors needed to provide "important leverage in overcoming the reliability and reproducibility problems" in the manufacture of ceramic components for heat engines. Strength and other performance properties are limited by process-related flaws. Flaws can result from undesirable characteristics of the powder and from manipulation of the powder into the pre-fired ("green") body. Improved characterization of ceramic powders requires not only greater accuracy and precision in measurement but also a better understanding of how powder characteristics are related to processing and performance of ceramic components.

Improvements in powders and powder characterization are expected to have a critical impact on the successful production of ceramic parts for heat engines. This market is expected to grow from a $56M in 1990 to $840M by the year 2000[2]. The International Energy Agency (IEA) recognized that powder characterization was among the critical factors for the development of ceramic heat engines when it established an international interlaboratory comparison of physical and chemical characterization methods for ceramic powders. This group is engaged in the preparation and certification of several thousand powder samples for this round-robin.

The market for electronic ceramics is expected to grow from $1,900M in 1990 to $3,485M in year 2000. Innovations in the use and control of powders are expected to offer a competitive edge in such areas of electronic ceramics as thin-layer electronic elements, substrates and mm-wave devices.

Understanding the connection between powder characteristics and processing and performance begins with the recognition that powders are complex physical and chemical systems in which characteristics are often spatially distributed within particles, between interior and surface, and between particles. An average value alone has little meaning for a characteristic of a powder. The distribution of a property between particles and within particles needs to be specified. There is a critical need for Standard Reference Materials (SRM's) with certified distributions to be used in the calibration and intercomparison of instruments for size distribution measurements.

The work of the group is carried out primarily in two laboratories: the Fine Powder Laboratory and the Automated X-Ray Diffraction Laboratory. This year a program was inaugurated to expand our capabilities in electron microscopy/image analysis.

Representative Accomplishments

- o 1500 zirconia powder samples and 9000 silicon nitride powder samples were prepared and certified for an international round-robin.

- o A synthesis method was developed for the preparation of alkali-stablized tridymite for a new x-ray diffraction SRM.

- o Ultrasonic measurements were used nondestructively to evaluate green, partially sintered and fully sintered alumina compacts containing hard and soft agglomerates.

- o A complete overhaul of the x-ray diffractometers was performed.

Powder Characterization

C. Robbins, J. Kelly, D. Minor, A. Dragoo, J. Sung (Student)

Research is carried out with a variety of methods, including x-ray sedigraph, photon correlation spectroscopy, Brunauer-Emmett-Teller (BET) surface area measurement, mercury intrusion porosimetry and density measurement. Powders are characterized as part of research efforts in ceramic processing, for studies of wear of ceramic components, and for certification of powders for interlaboratory comparisons and as Standard Reference Materials (SRM). Sources of variability in measurement of powder characteristics are being investigated for several alumina and silicon carbide powders. Preparation of samples of five ceramic powders for an international round-robin conducted under the auspices of the IEA has constituted a major effort in subdivision and packaging. The assurance of physical and chemical homogeneity between samples is critical to the success of the round-robin.

Electron Microscopy/Image Analysis

J. Kelly, D. Minor, A. Dragoo

Indirect methods of particle size measurement generally yield a size which is computed from a size-related phenomenon, such as sedimentation rate. The accuracy of indirect measurements depends on the validity of the algorithm used to compute the size and on the influence of other particle characteristics, such as shape, on the measurement. Direct characterization of particles can provide fundamental size and shape data to verify the physical assumptions underlying the indirect methods. For ultrafine particles scanning electron microscopy (SEM) and transmission electron microscopy (TEM) must be used to obtain high-resolution images. However, to achieve measurement standard errors of a few percent, on the order of 10,000 images may have to be measured. Consequently, automated image analysis is required. A program to expand our capability in this area was initiated this year.

X-Ray Diffraction

J. Cline, C. Hubbard, C. Robbins, A. Dragoo, Y. Zhang (Student), W. Wong-Ng*, H. McMurdie*, B. Paretzkin*, M. Morris*, E. Evans*, M. Mrose*

*JCPDS-ICDD Research Associates

The x-ray diffraction program includes the certification of SRM's, the investigation of material properties, such as residual stress, grain size and preferred orientation, and the generation of high-quality x-ray reference data for the Powder Diffraction File. Work on SRM's has focused on the recertification of two reference materials: SRM 640b, a silicon x-ray line position standard; and SRM 674, a set of five x-ray intensity standards. A synthesis method was developed for the preparation of alkali-stabilized tridymite which is being developed as a quantitative x-ray SRM. A workshop on Quantitative X-Ray Powder Diffraction Analysis, held on June 23 and 24, was attended by over 170 scientists from industry, government and academic laboratories. The need for new standards was emphasized in several technical presentations at the workshop. A new program was instituted with the International Centre for Diffraction Data (ICDD) for the production of powder diffraction patterns and data for important ceramic phases. This program replaces that of the JCPDS-ICDD Research Associated which over the past 30 years has produced many high-quality reference patterns.

Ceramic Processing

C. Robbins, M. Jones (Student), J. Kelly, D. Minor, A. Dragoo

The compaction and sintering of alumina powders consisting of hard and soft agglomerates were investigated by ultrasonic measurements of elastic constants. A technique was developed for dry-coupling the ultrasonic signal to the compacts. A correlation was observed between the elastic moduli and the density of the samples, with the samples formed from the hard agglomerates exhibiting lower values for the moduli and density in the green and partially sintered states. Green state compacts formed from both hard and soft agglomerates were observed to have negative Poisson's ratios. Measurements of porosity and surface area of these samples are in progress.

SURFACE CHEMISTRY AND BIOPROCESSES GROUP

Frederick Brinckman

The Group provides data essential for understanding and quantitating surface mechanisms of chemical and biological processes that are important in the processing, performance and durability of inorganic materials. For many materials molecular surface characterization is a prerequisite for control strategies based on molecular design. Current project areas include: quality control measurements for ceramic precursor powders, microbial processing of ores, performance of organotin antifouling coatings, and design of tailored phosphors and their performance on postage stamp surfaces. The Group's extensive experience and facilities in molecular chemical speciation in gas and liquid phases has guided our development of new facilities for surface molecular characterization of materials, as summarized in Figure 6.

The Group's critical measurement advances have now made possible the development of novel standards, especially in the areas of organotin speciation and microbial ore processing. Increasingly, the international community in these areas look to the Surface Chemistry and Bioprocesses Group for needed SRMs.

Representative Accomplishments:

- A novel epifluorescence microscopy imaging (EMI) method has been demonstrated, in collaboration with the Chemical Engineering Department at Johns Hopkins University, as an *in situ* probe for characterization of microbial metal ore processing on mineral surfaces. The technique is a valuable tool for obtaining a fundamental understanding of mechanisms of bioadhesion on refractory ore surfaces that affect bioengineering efficacy, in turn giving us a probe to monitor ore bioprocessing activity.

- Tributyltin (TBT) measurement methods and intercomparisons, environmental fate data, and standards have been delivered to the U.S. Navy in support of their implementation of organotin based antifouling coatings for the fleet. This unique information provides the Navy and other federal and state agencies with methodology for monitoring the marine environment, environmental fate data for hydrodynamic models, and research materials for interlaboratory intercomparisons and validations of the necessary measurements.

- Development of a novel, stable, water soluble phosphor for postage stamp tagging has been carried to the implementation stage in FY 1986. Our terbium complex eliminates the need for organic varnishes and heterogeneous abrasive inorganic phosphor particles in coating formulations, allowing for improved stamp visual quality and decreased wear on facer/canceller machinery.

- Diffuse reflectance Fourier transform infrared spectroscopy (FT-IR) is the basis for a rapid new measurement technique that quantitates the amount of β-phase present in bulk silicon nitride powder. Monitoring of % β-phase is necessary in Si_3N_4 quality control, and this effort demonstrates the potential utility of surface analysis in a wide variety of ceramic applications.

Materials Processing via Biotechnical Routes

G. J. Olson, F. E. Brinckman, T. Trout[1], H. Ehrlich[2], R. Blakemore[3],
J. S. Thayer[4], R. M. Kelly[5], W. P. Iverson[6]

[1]Graduate Co-op Student, University of Maryland
[2]Guest Scientist, Rensselaer Polytechnic University
[3]Guest Scientist, University of New Hampshire
[4]Guest Scientist, University of Cincinnati
[5]Guest Scientist, Johns Hopkins University
[6]Guest Scientist, NBS, emeritus

Facilities developed by the Group provide a unique capability to investigate and understand the fundamental mechanisms of bioprocesses for the selective dissolution and transformation of elements from metal ores and scrap. With U.S. Navy support we have demonstrated feasible bioleaching and biorecovery processes for strategic metals to provide new options for reducing National dependence on imported supplies. We are currently participating in the American Iron and Steel Institute -Federal Laboratory subcommittee on scrap steel recycling investigating novel bioprocesses for upgrading domestic iron ore (P, Si removal) and scrap steel (Cu removal) to improve the competitiveness of the U.S. steel industry.

The basic mechanisms of ore dissolution by acidophilic microorganisms have been poorly understood, mostly because measurements of microbial activity at ore surfaces are exceedingly difficult. With collaborators at Johns Hopkins University, we developed and demonstrated an EMI method to quantitate adhesion of ore processing bacteria to ore surfaces. This method employs acridine orange staining and epiillumination (440 nm) to indicate cell metabolic (metal releasing) activity based on fluorescence color of cells. The fluorescence color may be related to intracellular pH, indicating the metabolic state of the bacteria. Our data support the theory that organisms attached to ore surfaces are more important to ore dissolution than cells in free solution. Thus, the technique has important prospects not only for assessing processing status in leaching systems, but also for investigating fundamental scientific questions related to the mechanisms of metal ore dissolution by bacteria.

A significant barrier faced by the emerging bioleaching technology is the lack of standard substrates and standardized bioleaching testing procedures. New, more effective strains of leaching bacteria are being sought in the environment and developed in the laboratory by selective culturing or, in the future, genetic engineering. Consequently, we are working with OSRM to develop metal ore (sulfides) SRMs as standard substrates for bioleaching studies. In addition, the new ASTM Committee E-48 on Biotechnology formed a task group for developing standardized procedures for testing ore bioleaching with group member Olson serving as chairman. NBS SRMs will be important in interlaboratory comparisons of the standardized leaching procedures.

Finally, we applied our sensitive TBT speciation methodology to investigate the fate of TBT in its service (estuarine) environment. Lacking a measurement method, Navy models had assumed a relatively slow degradation (2% per day) of TBT in estuarine waters, causing concern about TBT persistence and effect on non-target biota. Concurrent work at NOSC and NBS has radically altered this picture of TBT persistence. We found TBT half lives of 1-2 weeks in estuarine water samples collected in summer. Algal activity accelerated the degradation to much less toxic di- and monobutyltin species. These data have altered the Navy model of TBT and suggest that at least during part of the year, TBT is biodegraded relatively rapidly to less toxic species in the environment.

Phosphor Coatings. The Group's expertise in molecular surface chemistry has successfully addressed a request by the U.S. Postal Service for improved, innovative postage stamp phosphor materials and processing technology. We have developed a method for tagging postage stamps wherein a homogeneous phosphorescent terbium coordination complex in aqueous solution is applied to paper substrates. Current tagging technology requires an abradible crystalline inorganic phosphor heterogeneously dispersed in organic varnishes. Our invention impinges directly upon the multi-billion dollar postage stamp industry, allowing for efficient cancellation, non-abrasion, and high quality, true-colored, varnish-free stamps.

The pure phosphor is readily synthesized in conventional apparatus. We have supplied several paper manufacturers with sufficient material for pilot plant scale paper preparations currently being field tested by NBS and USPS. Thus far the paper/phosphor combinations have shown excellent stability toward indoor and outdoor light exposure, and relative humidity conditions up to 90%. Under prolonged exposure to humidity in the 90-100% range however, phosphorescence efficiency declines. Two primary mechanisms contribute to phosphorescence loss: (1) solubility-induced migration of the terbium away from the stamp surface, and (2) coordination quenching via ligation of water to terbium.

The migration mechanism can be negated by molecular schemes that immobilize the phosphor at its intended surface location. Various chemical and coating strategies accomplish this goal. Quenching by water is a consequence of vibronic coupling between O-H stretching modes and the lowest excited state of the terbium complex, convincingly shown by the maintenance of stamp phosphorescence in a saturated D_2O atmosphere. Interestingly, however, 100% humidity conditions do not affect the phosphorescence of pure, crystalline terbium complex samples, indicating that different coordination environments exist around terbium in the crystalline state *vs.* on the cellulosic substrate.

Final data on paper/phosphor stability, toxicity, and economics are being gathered by USPS and NBS to facilitate implementation of the terbium phosphor as quickly as possible.

Interface Chemistry of Materials

W. R. Blair, E. J. Parks, G. J. Olson, R. A. Faltynek, F. E. Brinckman, T. Trout[1], E. Tierney[2], G. Eng[3], C. L. Matthias[2]

[1]Graduate Co-op Student, University of Maryland
[2]Guest Scientist, University of Maryland
[3]IMSE Faculty Appointment, University of the District of Columbia

Organotin Antifouling Materials. Regulatory decisions by the EPA in the next 2-4 years will affect marine use of TBT-based antifouling materials as well as U.S. Navy fleet plans to employ the innovative TBT-based antifouling polymer coatings, a strategy that would save hundreds of millions of dollars annually in fuel costs and enhance fleet preparedness. The Navy, EPA, NOAA, and other agencies conducting TBT risk-benefit assessments have found only limited environmental data, since measurement methods for the leached, toxic TBT species at action levels (ng L^{-1}) in the marine environment have not been available.

For many years the Group has had a world leadership position in developing measurement methods for the design, characterization, quality assurance and environmental fate of organotin materials. Group members serve on national (ASTM) and international (EEC-COIPM) committees evaluating organotin development, use and characterization. We have developed state-of-the-art methods for both quantitation of organotins and speciation of tributyltin and its degradation and redistribution products in seawater at necessary ng L^{-1} levels, transferred these techniques to the Navy, and trained Navy personnel for their monitoring program needs. EPA, industrial, and university laboratories are adopting NBS methodologies to initiate monitoring programs for aquatic systems. We also conducted with the Naval Ocean Systems Center (NOSC) a successful TBT measurement intercomparison and evaluation of storage procedures with field samples, demonstrating that reliable data intercomparisons of TBT concentrations in marine waters are now feasible.

Also important to the rapidly growing number of laboratories involved in tributyltin environmental monitoring world-wide is the availability of SRMs. Last year's report described a measurement methods intercomparison involving laboratories in 11 nations, employing a high purity, aqueous research solution of TBT generated chromatographically at NBS. Thus, we found that chromatographic synthesis of organotin solutions represents a reliable and reproducible method for producing very high purity solutions containing only a single molecular species, with good stability and shelf life, the attributes necessary for a SRM. We are currently producing, for the Navy, a mixed butyltin research material for another measurement intercomparison and will use the chromatographic generator column technique to produce speciated organotin SRMs. We plan to also use such generator column technology in the coming year to produce ultrapure ceramic precursors on a g-kg scale.

Molecular Structural Characterization of Ceramic Precursors

R. A. Faltynek, F. E. Brinckman, T. Trout[1]

[1]Graduate Co-op Student, University of Maryland

The ultimate quality of finished ceramic materials depends strongly on the purity and morphology of precursors used in their production. For example, silicon nitride powders prior to compacting, must contain an appreciable quantity of β-phase material to yield a product with acceptable physical properties. A survey of several silicon nitride powder samples from domestic and imported sources by diffuse reflectance Fourier transform infrared spectroscopy showed large intensity variances in the fingerprint bands assigned to β-phase bending modes between 750-550 cm^{-1}, with the strongest signal present in the sample known to produce the best finished ceramic. This prompted us to prepare a working curve correlating β-phase absorption with concentration that will allow for future rapid analysis of Si_3N_4 by FTIR (Figure 7). It is anticipated that other ceramic powders can be assayed for important functionality in the same manner, and that rapid, non-destructive infrared surface analysis by reflection techniques will become a significant part of ceramic quality control.

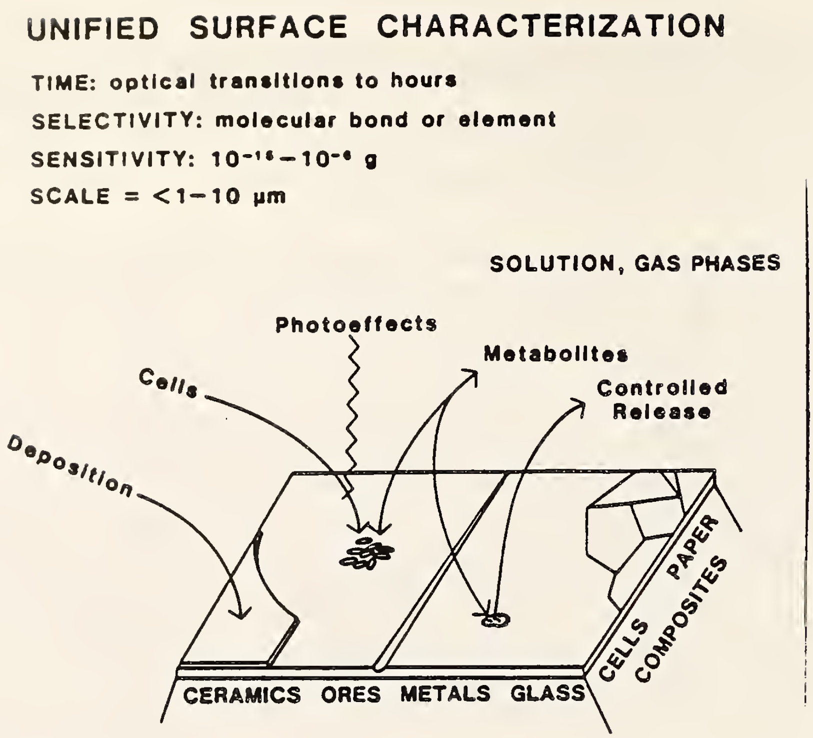


Figure 6. Ultratrace chemical speciation in gas and liquid phases is now integrated with newly developed Group capabilities in surface molecular characterization. FT-IR and computerized, quantitative epifluorescence microscopy together provide a unified molecular speciation capability for studying deposition or release of materials from surfaces involving chemical or biological processes.

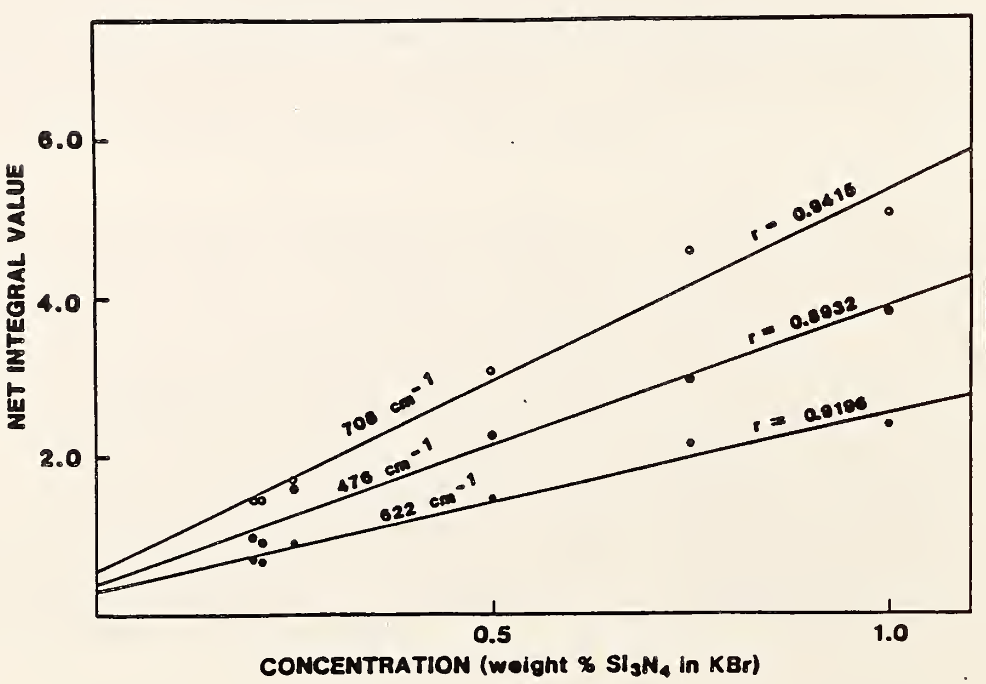


Figure 7. Absorbance vs concentration plots for 3 prominent infrared bands in microparticulate α, β phase silicon nitride, illustrating a method for non-destructive analysis of ceramic powder crystallinity by FTIR.

PROCESSING

STRUCTURAL SCIENCE

Edwin Fuller

The program of the Structural Science Group is focused on the structures of ceramic materials and on the relationship of these structures to the processes that formed them (ceramic processing) and to the properties and performance that these structures determine. Characteristic structural features of ceramic materials range from the molecular, or nanostructural scale to the microstructural level. Important features at the molecular level include crystalline defects (vacancies, interstitials, dislocations, etc.); interfaces and grain boundaries; and impurity chemical concentrations. At the microstructural level important features include grain size and morphology; second-phase inclusions and pores; cracks; reinforcing phases such as fibers and whiskers; and distributions of these entities.

Ceramic structures lie at the heart of surmounting the two major impediments to the production and use of advanced ceramic materials. The first of these impediments is the ability to capitalize effectively on the unique properties that advanced ceramics have, or the ability "to use what we have". The second is the ability, through an understanding of structure/property relationships, to tailor ceramic properties to a specific application, or the ability "to develop what we need". Knowledge of ceramic structures addresses both of these areas. Structures control the properties of ceramic materials and are determined by the ceramic processing. Understanding of these connections can lead to "mature", or well engineered materials and to effective ceramic design.

The research effort has two main areas: Fundamentals of Interfaces, and Structure/Property Relations. In the first area, interfacial properties, such as interatomic forces, surface and grain boundary energies, defect concentrations and formation energies, and impurity species are studied and related both to ceramic sintering and to brittle fracture. In the second area, the relations between microstructural features and fracture behavior are studied (toughening mechanisms at low temperature and creep rupture mechanisms at elevated temperature).

Representative Accomplishments

- An improved understanding of the importance of chemical composition on the sintering properties of ceramics through a comprehensive review of the literature. Key research opportunities have been identified, which has led to the design and development of an ultra-clean ceramic processing laboratory.

- Theoretical formulation using a lattice statics Green's function method to give a formally exact solution for the atomistic structure of grain boundary interfaces in ionic ceramics. The method fully accounts for the discrete structure of the lattice and uses the zero frequency limit of the phonon Green function.

- An improved technique for measuring and characterizing the strength of the interfacial bond between a ceramic reinforcing fiber and the ceramic matrix of a ceramic matrix composite using an instrumented Vickers hardness indenter.

Structures and Properties of Ceramic Interfaces

J. E. Blendell and C. A. Handwerker[1], E. R. Fuller, Jr., V. K. Tewary[2], C. A. Harding, and C. A. Shen

[1]Metallurgy Division, IMSE
[2]Guest Scientist, Birla Institute of Technical & Science, Pilani, India

The overall properties and performance of ceramic materials depend crucially on the structure and composition of interfaces in these materials. Understanding of these interface structures and their dependence on defects and composition is vital for the development of advanced ceramics with improved and tailored properties. Furthermore, as the demands made on these materials increase, and multiphase materials become technologically more important, the need for this basic understanding of interface structure and properties continues to grow. Several research areas in the Structural Science Group have been addressing these issues.

Interfacial Stability in Ceramics: Of particular importance to the properties and performance of advanced ceramic materials, both during the processing steps that forms them and during use in service, is the stability of the boundaries and interfaces in these materials. Diffusion induced grain boundary migration (DIGM) is a mechanism by which otherwise stable boundaries can be induced to migrate, due to the diffusion of a solute into or out of the material. Thus it is a process that needs to be understood in order to obtain optimum performance from high technology materials.

In the past year DIGM has been studied in both alumina and magnesia. The samples have been annealed in the presence of various solutes in order to induce boundary migration. The experimental conditions have been selected to test a current model for DIGM, which assumes that the driving force for migration is the differential strains and strain energy that is developed during the diffusion.

Structure and Energy of Ceramic Grain Boundaries: Theoretical studies have been undertaken to elucidate the structure and energy of ceramic grain boundaries and their dependence on defects and chemical composition. This research has been conducted in collaboration with a guest worker from the Birla Institute of Technology and Science, Pilani, India. A formally exact solution for the atomistic structure of grain boundary interfaces has been obtained for ionic ceramics using a lattice statics Green's function method. The method fully accounts for the discrete structure of the lattice and uses the zero frequency limit of the phonon Green function. This is in contrast to previous calculations which have used finite clusters of atoms, or are matched to continuum solutions, and thus depend critically on the boundary conditions.

The grain boundary is taken along coincidence lattice sites which are obtained by rotating two imaginary halves of a crystal relative to each other. Perfect translation symmetry is assumed along the grain boundary line. This periodicity is exploited by taking a partial Fourier transform of the Green function. The long-range Coulombic interactions between ions across the grain boundary have been shown to be effectively dipolar and higher order polar interactions which makes them relatively short range. Thus far, the method has been applied to a tilt boundary in the ionic rock-salt structure of MgO with a simplistic two-body potential.

Sintering of Ceramics

J. E. Blendell, C. A. Handwerker[1], C. P. Ostertag[2], E. R. Fuller, Jr., C. A. Harding, and C. A. Shen

[1]Metallurgy Division, IMSE
[2]Guest Scientist, University of California, Santa Barbara

Impurity Effects: It is well known that impurities can dominate the sintering and microstructural development in ceramics. However, there is a lack of quantitative understanding of the mechanisms by which impurities affect sintering. In order to study the effect of impurities it is necessary to produce ceramic powders and compacts with documented low levels of impurities. This requires the use of clean room processing techniques and the ability to measure the impurity levels in the samples.

A laboratory for clean room processing has been designed and is being constructed. This will be used to produce powders with low levels of impurities. The impurity concentrations of the powders will be measured and the contamination during processing will also be documented. This is necessary as it is the impurities present during sintering that affect the microstructure, and significant impurities can be introduced during compaction, calcination and sintering.

Grain Growth in the Presence of a Liquid Phase: The presence of a liquid phase during sintering, which is common in commercial ceramic materials, changes the grain morphology and the rate of grain growth. To study this effect, a known amount of a liquid phase (anorthite) was added to alumina compacts which contained large single crystal sapphire spheres. The grain growth rate of both the matrix grains and the large spheres were measured. It was found that the presence of the liquid phase changed the shape of the growing grains as compared to the grains when no liquid was present. Also, while the presence of a liquid phase lowered the grain growth rate, the addition of MgO reduced the grain growth rate even more. These results give insight into the microstructure development when impurities are present.

Interfaces in Ceramic Matrix Composites

T. W. Coyle, E. R. Fuller, Jr., C. P. Ostertag[1], R. F. Krause, Jr., S. W. Freiman[2], and A. Gilat[3]

[1]Guest Scientist, University of California, Santa Barbara
[2]Glass and Composites Group
[3]Guest Scientist, "RAFAEL" Armanent Development Authority, Israel

The low and high temperature mechanical performance and structural stability of ceramic matrix fiber composites is controlled to a large extent by the structure, properties and stability of the fiber-matrix interface. Techniques to characterize these interfacial properties and relate them to the micro- and macro-scale mechanical behavior are required to develop reliable ceramic composites. The experimental studies have been undertaken to develop the understanding necessary to bridge the gap between the nature and behavior of the fiber/matrix interface and the performance of the bulk composite material.

Three scales of behavior are examined: the mechanical behavior of the fiber/matrix interface of individual fibers is characterized by an indentation technique utilizing an instrumented hardness indenter; the interaction of matrix cracks with simple arrays of fibers is investigated through the use of fracture mechanics specimens yielding controlled fracture behaviors; and the performance of bulk composites (uniaxial and woven fiber reinforced materials and whisker toughened materials) is examined in flexural, tensile and shear failure modes. The performance of bulk composites are further characterized by examination of the creep behavior and related stress redistribution that occurs under load at high temperature.

Stress Induced Phase Transformations

T. W. Coyle, S. Block[1], G. J. Piermarini[1], and R. P. Ingel[2]

[1]Structural Chemistry Group
[2]U. S. Naval Research Laboratory

Transformation toughening is now a well-known and effective method for improving the fracture behavior of ceramic materials. Further understanding of the possibilities and limitations of the transformation toughening mechanism requires a better understanding of the thermodynamics and kinetics of the transformation itself. Studies designed to examine the influence of mechanical versus chemical driving forces on the transformation behavior of ZrO_2 have been initiated. These include: Raman microprobe analysis of the phase composition in regions of high local stress arising from residual stresses and in-situ analysis under applied stress; an informal collaboration with R. P. Ingel of the Naval Research Laboratory to examine the high temperature mechanical behavior of skull-melt grown crystals of unstabilized ZrO_2; and studies of the pressure dependence of the stability of the various phases present in doped and undoped ZrO_2 in collaboration with Block and Piermarini of the Structural Chemistry group.

CERAMIC CHEMISTRY **Kay Hardman-Rhyne**

Research and development in ceramics for structural, optical, electronic, magnetic, and other applications is being directed increasingly toward improvements in processing science that will permit reproducible production of defect-free materials. This goal requires extremely sophisticated microstructural control. It is now recognized that the evolution of microstructure begins at the very earliest stages of processing, in the chemistry of powder synthesis, and is carried forward in the subsequent compaction and densification stages to finished ceramic bodies. New approaches to ceramic synthesis are evolving, based on advanced molecular-level synthetic, mechanistic, and structural chemistry. Low-temperature synthetic procedures, such as the "sol-gel" processes, are becoming increasingly important for synthesis of advanced materials, often in heretofore unattainable compositions. Advanced structural techniques, such as SANS and high-resolution electron microscopy, are being utilized increasingly to elucidate the pathways by which molecular structures evolve into ceramic structures and microstructures.

The program of the Ceramic Chemistry Group is focused on research to facilitate the application of modern chemical techniques and understanding to improved processing of ceramics. The Group's goal is essentially to put more and better chemistry into ceramic processing. The objectives of the group are to provide data, measurement methods, concepts, and standard materials relating to chemical aspects of ceramics processing needed by industry for predictive control of new processes and development of new materials. Current emphasis is on advanced synthetic methods, evolution of structure in ceramic synthesis, and relation of chemical process variables to particle characteristics and microstructure.

Representative Accomplishments

- Generation of SiC, TiB_2, and B_4C from precursors prepared at 130°C in 85-90% yield.

- Generation of particulate composite materials including SiC/TiC and SiC/TiN from low-temperature precursors.

- Application of SAXS, SANS, and chemical techniques to characterization of structure evolution in sol-gel processing.

Low-Temperature Chemical Processing Routes to Boride and Carbide Ceramics Powders

J. J. Ritter and N. K. Adams

Conventional procedures for generating boride and carbide ceramic powders are conducted at temperatures in excess of 1500°C. However, the control of powder purity, particle size and size distribution is difficult under these conditions. A novel low temperature chemistry has been developed which permits the synthesis of precursors to boride and carbide ceramic powders in a controlled fashion at only 130°C. For example, it has been shown that

$TiCl_4$ and BCl_3 react with sodium at 130°C in a non-polar solvent to give the precursor to TiB_2. Similar type reactions with $SiCl_4$ and CCl_4 or BCl_3 and CCl_4 have produced the precursors to SiC and B_4C repectively. The technique has been extended further to the syntheses of precursors to particulate composites such as SiC/TiC and SiC/TiN. The highest powder yields are obtained from reactions conducted in a special NBS designed, hermetically sealed, high shear reactor shown in Figure 8. As precipitated, the precursors, are amorphous materials which require further heat treatments for crystallization. Moreover, the chemistry can be extended to any combination of metal, non-metal or metalloid halides which can be reduced by alkali metals. Thus, a wide variety of metal-metal, metal ceramic and ceramic-ceramic materials are accessible through this procedure.

Structural Evolution in Low-Temperature Ceramic Processing

T. D. Coyle, K. Hardman-Rhyne, and E. P. Lewis

Although low-temperature synthesis of ceramic powders and glasses offers numerous advantages, its use has been largely empirical. A new research program has been initiated to elucidate the fundamental reaction mechanisms by which structure evolves in low temperature processing from molecular precursors to glass or crystalline products in multicomponent systems. The objective of the work is to define the critical chemical parameters that will permit predictive control of powder, film and glass processing. Current research emphasizes processes for synthesis from metal-organic precursors of multicomponent oxide-systems of interest as electronic or dielectric materials. Molecular structure and kinetics are being studied, by GC, spectroscopy (FTIR, NMR); the polymerization of molecular species to amorphous ceramic precursors and densification of sol-gel derived materials is being evaluated by SANS methods; and crystallization of amorphous precursors is being studied by conventional x-ray diffraction techniques.

During the past year the first combined use of SAXS and SANS, along with chemical techniques, has been applied to structure development kinetics during sol-gel synthesis of silica precursors. Insights into the kinetic processes have been obtained by the use of deuterated materials.

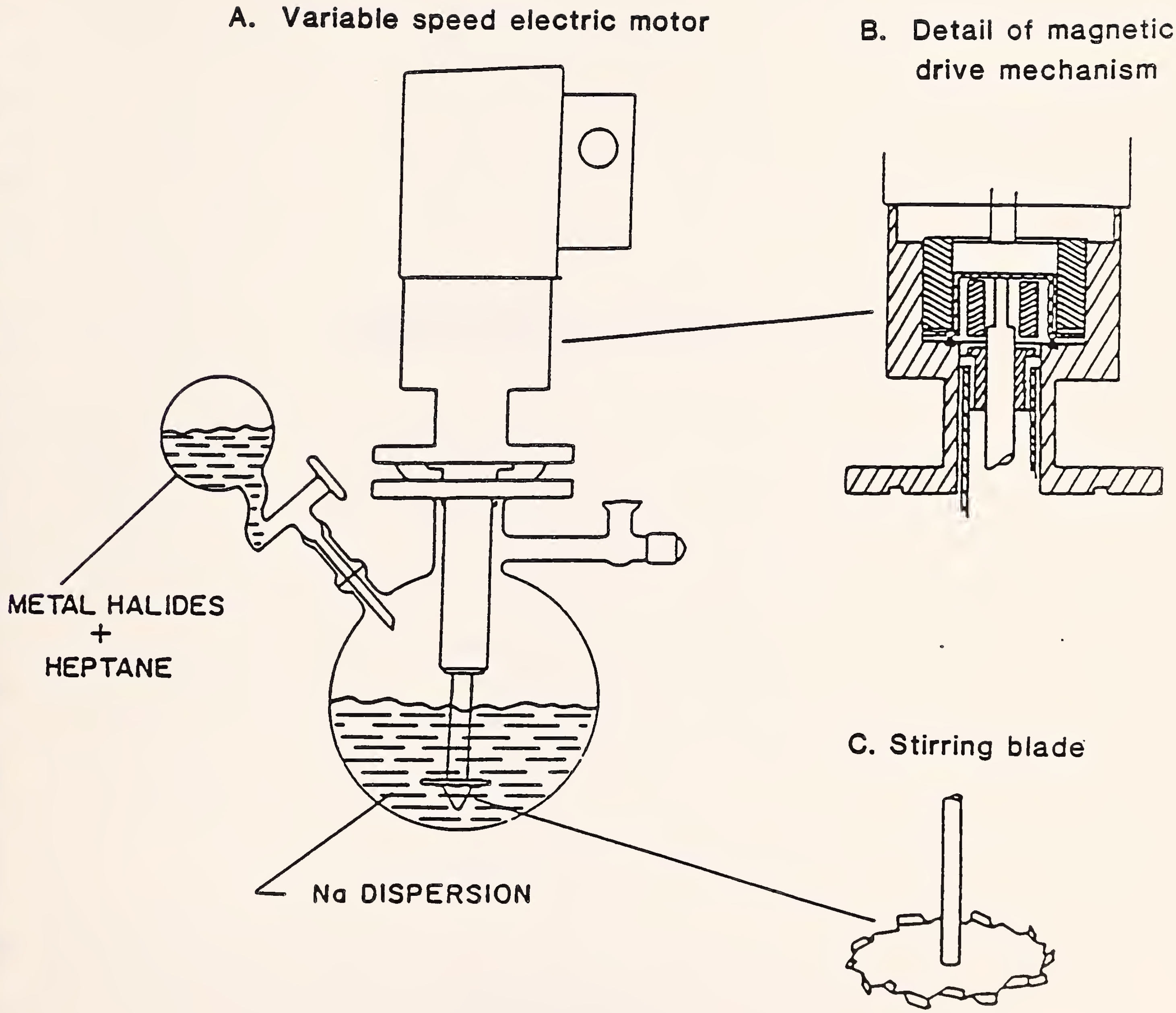


Fig. 8. Magnetically coupled, high-shear chemical reactor.

RESEARCH STAFF

PROPERTIES/PERFORMANCE

Mechanical Properties

Chuang, Tze-Jer	o Ceramics o Diffusional crack growth o Finite element analysis o Creep theory
Chuck, Leon	o High temperature mechanics o Scanning electron microscopy o Acoustic monitoring of cracks
Fairbanks, C. J.	o Microstructure/strength relations
Hockey, Bernard	o Ceramics o Deformation and wear o Scanning and transmission electron microscopy
Lawn, Brian R.	o Microstructure/strength relations o Fracture mechanics o Contact phenomena o Surface forces in fracture
Roach, David	o Surface forces in fracture o Fracture mechanics
Tighe, Nancy	o Ceramic creep o Microstructural analysis o Scanning and transmission electron microscopy
Wiederhorn, Sheldon M.	o Ceramics o Fracture processes o Mechanical properties at high temperature and pressures

Glass and Composites

Blackburn, Douglas H.	o Special glass formulations o Glass processing o Glass standards for microprobe analysis
Cellarosi, Mario J.	o Glass SRM development o Glass standards for manufacture and use o Glass property measurements
Freiman, Stephen W.	o Ceramics and glasses o Fracture mechanics o Mechanical properties, environmental effects

Inglehart, Loretta L.	o Thermal wave analysis o Nondestructive evaluation o Ceramic materials
Swanson, Peter L.	o Ceramic fracture o Microstructure o Geologic materials
White, Grady S.	o Ceramics and glass o Nondestructive evaluation o Subcritical crack growth

Tribology

Gates, Richard	o Friction and wear of materials o Wear mechanisms and analysis o Engine condition monitoring o Ferrography
Hegemann, Bruce E.	o Laser-Raman spectroscopy o Ultra-fast microwave detection o Trace laser analysis techniques o Heterogeneous catalysis
Hsu, Lin-Sien	o Lubricant volatility o Oxidation stability o Lubricant fractionation o High temperature lubrication
Hsu, Stephen M.	o Tribology o Oxidation mechanisms of organic mixtures o Lubrication and wear mechanisms o Molecular structural effects on friction o High temperature ceramic wear
Jewett, Kenneth L.	o Organometallic speciation o Oxidation kinetics o Analysis of organic mixtures o SRM research
Ku, Chia-Soon	o Oxidation kinetics o Friction and wear test development o Modeling of reaction systems o Kinetics of volatility in lubricants
Munro, Ronald G.	o Theory and modeling o Tribology o Molecular dynamics of phase stability o Temperature modeling of ceramic pairs
Pei, Patrick	o Separation of complex organic mixtures o Trace organic compound identification o Differential scanning calorimetry

Optical Materials

Farabaugh, Edward N.
- Thin film deposition and analysis
- X-ray diffraction analysis
- Scanning electron microscopy
- Surface analysis

Feldman, Albert
- Optical materials
- Thin films
- Solid state physics
- Photoelasticity and thermo-optics
- Guided waves
- EXAFS

Frederikse, Hans P. R.
- Electrical and mass transport in solids
- Electrical conductivity
- Depth profiling (Rutherford backscattering)
- Thermal wave analysis

Steiner, Bruce W.
- Calorimetric absorption
- X-ray topography

STRUCTURE/STABILITY

High Temperature Chemistry

Bonnell, David W.
- High temperature-pressure mass spectrometry
- Computer modeling
- Levitation calorimetry

Cook, Lawrence P.
- Phase equilibria of ceramics (modeling and experiment)
- Phase diagrams for ceramists data center
- Electron microscopy
- Thermodynamics

Davidson, Paula M.
- Phase equilibria models
- Thermodynamics

Hastie, John W.
- High temperature chemistry of ceramics
- Ceramic phase equilibria and solution models
- High temperature-pressure mass spectrometry
- Chemistry of combustion

Ondik, Helen M.
- Phase diagrams for ceramists data center
- Materials properties for coal conversion
- Data compilation systems

Plante, Ernest R.
- High temperature chemistry of ceramics
- Knudsen effusion mass spectrometry
- Vaporization thermodynamics

Roth, Robert S.
- o Crystal chemistry of ceramic materials
- o Phase equilibria
- o Dielectric and ionic conducting ceramics
- o Phase diagrams for ceramists data center

Schenck, Peter K.
- o Laser spectroscopy
- o Temperature measurement
- o Computer graphics

Structural Chemistry

Block, Stanley
- o Properties, structure and polymorphism of materials at pressure
- o Ultra high pressure properties
- o Crystallography and pressure phase relations of ceramics
- o Generation/measurement of high pressures

Piermarini, Gasper J.
- o Pressure/temperature effects on ceramic materials
- o Generation/measurement of high pressures
- o Physical and structural properties of materials at high pressures and temperatures
- o X-ray diffraction, phase relations, optical measurements

Ceramic Powder Characterization

Cline, James P.
- o X-Ray diffraction of ceramics
- o Quantitative analysis

Dragoo, Alan L.
- o Characterization of ceramic precursor powders
- o Chemical bonds in solids
- o Ceramic powder synthesis

Hubbard, Camden R.
- o Crystallite size and residual stress
- o Quantitative x-ray diffraction methods
- o X-ray diffraction standard reference materials
- o Reference powder patterns (JCPDS Research Associateship)

Kelly, James F.
- o Scanning electron microscopy
- o Image analysis
- o A-C spectroscopy

Minor, Dennis B.
- o Analytical SEM of ceramics and particulates
- o Ceramic composites
- o High temperature ceramic synthesis

Robbins, Carl R.	o Fine ceramic particulate properties and characterization o Spray drying; powder preparation o Quantitative microscopy and x-ray diffraction o NDE of ceramics

Surface Chemistry and Bioprocesses

Blair, William R.	o Ultratrace metals speciation o Biotransformations of metals o Environmental durability of coatings o Molecular surface characterization
Brinckman, Frederick E.	o Environmental metal transport o Organometallic chemistry o Biological mediation of surface chemistry o Ultratrace metal speciation o Materials durability
Faltynek, Robert A.	o Inorganic molecular synthesis o Surface and solution photochemistry o Spectrophotometry o Heterogeneous catalysis
Olson, Gregory	o Metals biotransformation o Bioprocessing industrial materials o Epifluorescence microscopy imaging o Surface modification and bioadhesion
Parks, Edwin J.	o Metalloorganic synthesis o Macromolecular organometallic chemistry o Metals imaging in coatings o Ultratrace metal speciation o Controlled-release and bioactive polymers

PROCESSING

Structural Science

Blendell, John	o Ceramic processing and sintering o Sol-gel chemistry o Diffusion controlled processes o Activation analysis
Coyle, Thomas W.	o Processing/Microstructure/fracture relationships o Stress induced transformations o Toughening mechanisms in ceramics

Fuller, Edwin R.	o Atomistic models of fracture and grain boundaries o Fracture mechanics of ceramics and composites o Fracture, environment-assisted o Mechanical properties at high temperature o Nondestructive evaluation
Krause, Ralph F.	o Fracture mechanics of ceramics o Creep of ceramics o Chemical equilibria o High pressure and high temperature conditions

Ceramic Chemistry

Coyle, Thomas D.	o Inorganic and organometallic chemistry o Chemistry of materials processing and durability o Low temperature synthesis of ceramic powders o Chemistry of ceramic precursor materials
Frase, Katharine G.	o Electrical properties o Ceramic powder synthesis and processing o Neutron scattering
Lewis, Era	o Ceramic processing o Colloid and sol-gel chemistry o Small angle neutron scattering
Rhyne, Kay A.	o Ceramic processing o Neutron scattering o Nondestructive analysis o Colloid and sol-gel chemistry
Ritter, Joseph J.	o Synthetic inorganic chemistry o Ceramic powders from organometallic precursors o Ceramic powders from gas phase, and solution precipitation reactions

GUEST SCIENTISTS AND GRADUATE STUDENTS

Mechanical Properties

GUEST SCIENTISTS

Bennison, S., Mr. (Lehigh U)	o Strength and microstructure of ceramics.
Carroll, D., Dr. (Penn State U.)	o Creep and creep rupture of ceramics.
Chan, H., Dr. (Lehigh U.)	o Strength and microstructure of ceramics
Chen, C.F., Mr. (Univ. of Mich.)	o Deformation and fracture of silicon nitride.
Lathabai, S., Dr. (Lehigh U.)	o Strength and microstructure of ceramics
Sun, J., Ms. (Shanghai Inst. of Ceramics)	o Element analysis of structural ceramics

Glass and Composites

GUEST SCIENTISTS

Deshmukh, P., Dr. (Drexel U.)	o Ceramic matrix composites - processing and property determination
Gilat, A., Mr. (Israel Ministry of Defense)	o Fracture behavior of various fiber reinforced ceramics
Greenspan, D., Dr. (Accumetrix Corp).	o Relation between surface reaction and crack growth
Inglehart, L., Dr. (Johns Hopkins)	o Develop laser thermal wave lab

Legal LeSalle, E., Mr. (ESPCI)	o Assemble and establish a thermal wave imaging lab
Palamides, T. Mr. (Drexel U.)	o Ceramic matrix composites, processing and property determination

GRADUATE STUDENTS

Gonzalez, A. (Penn State)	o Time dependant failure
Nguyen, V. (U. of PA)	o Thermal wave analysis

Tribology Group

GUEST SCIENTISTS

Danyluk, S., (Prof. U. of IL)	o Mechanical and environmental effects in the wear of ceramics
Jahanmir, S., Dr. (NSF)	o Research on physics and chemistry of interacting surfaces
Klaus, E., Dr. (Penn State U.)	o Lubricant and additive chemistry
Lim, D., Dr. (U. Of IL)	o Wear mechanisms in ceramic pairs
Peussa, J., Dr. (Helsinki U.)	o Wear of ceramics under boundary lubrication conditions
Wang, Fu-Xing, Dr. (U. of Tsinghua)	o Wear mechanisms in ceramics pairs

GRADUATE STUDENTS

Bailey, D. (Penn State U.)	o Chemiluminescence and tribochemistry

Deckman, D. (Penn State U.)	o Vapor phase lubricaton at high temperatures
Yellets, J. (Penn State U.)	o High temperature tribometry

Optical Materials

Gomez-Barengo, R., Mr. (Inst. Politecnico-Mexico)	o Optical properties of thin films
Guenther, K., Dr. (U. of Alabama)	o Thin film deposition and characterization
Laor, U., Dr. (Nuclear Res. Ctr.-Negev, Israel)	o Research in crystalline optical materials
Sun, Y., Mr. (Lanzhou Inst. of Physics, Peoples Republic of China)	o Thin films and surface analysis

High Temperature Chemistry

GUEST SCIENTIST

Cava, R., Dr. (Bell Labs)	o Location of light elements in heavy metal oxides by neutron diffraction
Chang, L., Dr. (U. of MD)	o Experimental phase equilibria in molybdate and tungstate systems and also sulfides
Davies, P., (U. of PA)	o Defects in microwave dielectric materials
Parker, H., Dr. (NBS/ACers)	o Assist in compilation, editing, and associated activities in support of the Phase Diagram Data Center
Zmbov, K. Dr. (Boris Kidrich Inst.)	o Investigate the phenomenom of temperature dependent mass spectrometry

STUDENTS

Davis, K. (U. of MD)	o Synthesis of materials for high pressure phase transformation studies

Ceramic Powder Characterization

GUEST SCIENTISTS

Domingues, L., Mr. (Trans Tech, Inc)	o Process experimental precursor ceramic powders and green compacts
Stewart, J., Dr. (U. of MD)	o X-ray characterization
Zhang, Y., Mr. (U. of MD)	o X-ray characterization

STUDENT

Sung, J. (Cornell U.)	o Powder characterization and image analysis

Surface Chemistry and Bioprocesses

GUEST SCIENTISTS

Blakemore, R., Dr. (U. of NH)	o Ferromagnetic materials, investigate Co and U uptake, metal transformations
Bretz, M. Dr. (U. of Md.)	o Sol-gel processing - fractal development in silicon gels
Kelly, R., Dr. (Johns Hopkins U.)	o Investigation into the attachment and bacterial solubilization of metal ores for bioengineering
Matthias, C., Ms. (U. of MD)	o Design, develop, and implement ultra trace molecular measurement methods

Thayer, J., Dr. (U. of Cincinnati)	o Investigate bio-methylation and solubilization of metal-containing sediments and strategic ores
Tierney, E., Ms. (U. of MD)	o Develop and apply multi-element specific molecular measurement methods

GRADUATE STUDENT

Trout, T., Mr. (U. of MD)	o Metals bioprocess monitoring, organometallic photochemistry

RESEARCH ASSOCIATES

Degnan, T., Dr. (Mobil Oil)	o Fossil fuel processing
Eng, G. Prof. (U of DC)	o Theoretical and experimental applications of molecular topology for predicting chemical reactivity

Structural Science acd Chemistry

GUEST SCIENTISTS

Craig, C., Mr. (DOD)	o Creep studies of various ceramic materials
Frase, K., Dr. (IBM)	o Collaboration on small angle neutron scattering and ceramic powder synthesis, and characterization, and SANS
Miller, P., Mr. (Naval Surface Weapon Ctr)	o Pressure dependence of the spectra of high energy materials
Ostertag, C., Dr. (U. of CA, Santa Barbara)	o Collaborative research in ceramic processing
Ritter, A., Mr. (Martin Marietta Lab)	o Processing of ceramic composites
Tewary, V., Dr. (Ohio State)	o Calculating grain-boundary structures and energies in ceramic materials

Vandiver, P., Dr. (Smithsonian Conserv. Analytical Lab)	o Phase equilibria and corrosion studies of multicomponent ceramic systems
Vaudin, M., Dr. (Cornell, U.)	o Microscopy and diffraction of ceramic interfaces
Winzer, S. Dr. (Martin Marietta Lab)	o Ceramic processing of composites

OUTPUTS AND INTERACTIONS

SELECTED RECENT PUBLICATIONS

Mechanical Properties Group

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Glass and Composites Group

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Tribology Group

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Optical Properties Group

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High Temperature Chemistry Group

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Murphy, D. W.; Cava, R. J.; Rhyne, K.; Santoro, A.; Zahurak, S. M.; Dye, J. L.; Roth, R. S. Structural aspects of insertion reactions of the pyrochlore, $KNbWO_6$. Solid State Ionics 18, 19: 799-801; 1986.

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Structural Chemistry Group

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Ceramic Powder Characterization Group

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Structure Science Group

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Ceramic Chemistry Group

Berk, N. F.; Hardman-Rhyne, K. A. The phase shift and multiple scattering in small angle neutron scattering: application to beam broadening for ceramics. Physcia; 136B: 218-222; 1986.

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SELECTED TECHNICAL/PROFESSIONAL COMMITTEE LEADERSHIP

American Ceramic Society
- Glass Division
  - S. W. Freiman, Chairman
  - Committee on Glass Standards Classification and Nonmenclature
    - M. J. Cellarosi, Chairman
  - Editorial Committee
    - S. Wiederhorn, Subchairman
- Basic Science Division
  - Editorial Committee
    - B. R. Lawn, Chairman
    - A. L. Dragoo, Subchairman

American National Standards Institute (ANSI)
- Committee 43.1--Safety Standards for X-ray Diffraction and Fluorescence Analysis Equipment
  - S. Block, Chairman

American Physical Society Editorial Board
- Review of Scientific Instruments
  - P. K. Schenck

American Society for Metals
- Energy Division Fuel Manufacturing Committee
  - S. J. Dapkunas, Subcommittee Chairman
- Journal of Materials for Energy Systems
  - S. J. Dapkunas, Associate Editor

American Society for Testing and Materials
- C14: Glass and Glass Products
  - M. J. Cellarosi, Chairman
  - C14.01: Nomenclature of Glass and Glass Products
    - M. J. Cellarosi, Chairman
- F1: Electronics
  - F1:02: Laser
    - A. Feldman, Subcommittee Editor
  - D2: Petroleum Products and Lubricants
    - D2.09G: Oxidation
    - S. M. Hsu, Chairman
    - C. S. Ku, Member
  - E29: Particle Size Measurement
    - E29.01: Advanced Ceramics, Organizational Meeting
    - M. J. Cellarosi
  - E48: Biotechnology
  - E48.03.07: Bioleaching of Ores
    - G. J. Olson, Task Group Chairman

American Society of Lubrication Engineers
    Annual Meeting Program Committee
        S. M. Hsu, Secretary
    Committee on Wear
        S. M. Hsu, Chairman

COMAT Subcommittee on Ceramics
    S. M. Hsu, Member

Department of Energy
    Materials Review Board for Nuclear Waste
        H. P. R. Frederikse, Member

Gordon Research Conference on Tribology
    S. M. Hsu, Vice Chairman

Gordon Research Conference on Solid State Studies in Ceramics
    B. R. Lawn, Chairman

High Temperature Science Editorial Advisory Board
    J. W. Hastie

Interagency Coordinating Committee on Ceramics
    S. M. Hsu, Member

International Energy Agency
    Task II - International Standards
        Assignment II-O-1 Powder Characterization Working Group
            A. L. Dragoo, Member

International Commission for Optics
    U. S. National Committee
        B. Steiner, Chairman

International Union of Crystallography (IUCr)
    Commission on Crystallographic Studies at Controlled
    Pressures and Temperatures
        G. J. Piermarini, Chairman

International Union of Pure and Applied Chemistry
    Commission II-3: High Temperature and solid State Chemistry
        J. W. Hastie, U.S.A. Associate Member

JCPDS-International Centre for Diffraction Data
    C. R. Hubbard, Vice-Chairman

NAS Assessment Committee on Ceramic Tribology
    S. M. Hsu, Member

National Academy of Sciences/National Research Council
    Solid State Sciences Panel
        H. P. R. Frederikse, Member

National Aeronautics and Space Administration
High Temperature Advisory Committee
D. W. Bonnell, Member

Oak Ridge National Laboratory
High Temperature Materials Laboratory Advisory Committee
S. M. Wiederhorn, Chairman

Off-Road Machinery Technology Steering Committee, Wear Task Group
S. M. Hsu, Member

Optical Society of America
1985 Annual Meeting Local Arrangements Committee
B. Steiner, Chairman

INDUSTRIAL AND ACADEMIC INTERACTIONS

The Ceramics Division actively participates with Industry Academia and other Government Laboratories in research programs of mutual interest. The following examples are illustrations of this interaction.

INDUSTRIAL

1. Accumetrix Corporation

   H. P. R. Frederikse is collaborating with Dr. David Greenspan of Accumetrix Corporation to study the thermal and adhesive properties of plasma sprayed ceramic films. The films are prepared at Accumetrix and their properties are measured by means of photothermal radiometry. The research is expected to result in means for monitoring the production quality of ceramic coatings.

2. American Ceramic Society

   The High Temperature Chemistry Group interacts with the Ceramics Industry, through the Joint NBS/ACerS Phase Diagrams for Ceramists Program. The ceramics industry provides information to NBS on phase diagram needs and priorities through their participation in ACerS-NBS Committees and through direct interactions (visits) between industrial and NBS management and technical personnel. The industry is also funding a Ceramic Society program for Research Associateships to expand the NBS Data Center on ceramic phase diagrams. The Ceramic Society publishes and disseminates the Data Center outputs which have included five hard-cover volumes containing 6500 evaluated phase diagrams, and which in the future will also include on-line computer services to industry.

3. American Iron and Steel Institute

   The High Temperature Chemistry Group interacts closely with the U.S. steel industry through participation in the AISI national Task A committee (Ore to Steel Conversion), and technical collaboration with various steel industry R and D personnel. A preliminary thermochemical model for steel slag-refractory phase equilibria has already been provided to Inland Steel.

4. G. J. Olson of the Surface Chemistry and Bioprocesses Group is a member of the AISI - Federal Laboratory Task A subcommittee on scrap recycling. The Group is also examining upgrading of ores and concentrates via biological phosphorus, silicon, and sulfur removal.

5. AT&T Bell Laboratories

Research on the crystallographic characterization of ionic ceramic conductors is being carried out in a collaborative program between R. J. Cava and D. W. Murphy of Bell Laboratories and A. Santoro (Reactor Division) and R. S. Roth. Lithium inserted oxides are prepared at Bell Labs and characterized at NBS using the neutron diffraction total profile (Rietveld) analysis. The neutron diffraction data and analysis techniques uniquely locates the position of the lithium ion in the structure. Current emphasis of the joint work is on alkali niobium-tungsten-vanandium oxide phases having the pyrochlore type structure.

6. ARCO Chemical Co. - Dr. James F. Rhodes

Microstructural and structural characterization of ceramic matrix composites correlating mechanical properties to microstructural properties and to processing conditions.

7. Atlantic Mining Company

The Surface Chemistry and Bioprocesses Group is carrying on a research collaboration with AMC to characterize biological processes potentially useful for recovery of precious and strategic metals from certain major domestic deposits, of low grade pyritic ores. These ores are not amendable to conventional processing due to matrix effects and low grade nature of the deposits. In addition to selective bioextraction of noble metals, platinum and gold for example, new bioreactor designs are being evaluated for improving iron processing.

8. AVX Corporation

S. W. Freiman and T. L. Baker of the Glass and Composite Group are working closely with Dr. Bharat Rawal of AVX on a program to understand the mechanical properties of multilayer ceramic capacitors. AVX is preparing specimens of differing composition and properties. These are subsequently tested at NBS.

9. Battelle Memorial Institute

B. Steiner has worked closely with Battelle Memorial Institute in identifying areas for close technical collaboration in support of a multiclient program that Battelle is assembling to develop electrooptic technology for optical communications. Initial research has begun in collaboration with the Center for Analytical Chemistry in the analysis of single crystals of lithium niobate. Parallel synchrotron topographic studies will be initiated shortly.

10. Bundesanstalt fur Materialprufung, Berlin W. Germany

NBS/BAM Symposium on Materials Research and Testing: Ceramic Materials

11. Crystal Technology, Inc.

B. Steiner and the Synchrotron Group of the Metallurgy Division have collaborated with Crystal Technology on monochromatic topographic examination of specially grown lithium niobate single crystals during the first two weeks of dedicated x-ray ring operation at the National Synchrotron Light Source. Crystals grown under various conditions display highly growth-dependent defects and strains. Such defects can affect the fabrication of complex communications and computing devices made from these crystals. Correlation of the topographic information with parametric variation in the crystal growth process will help to separate those defects associated with the initial crystal growth from those associated with subsequent diffusion to form waveguides in the crystal.

12. Dupont Corporation

Cooperation between Ceramic Chemistry Group and industrial laboratories (DuPont, DOW) using SANS to characterize powder agglomeration in AlOOH and ZnO.

13. Georgia Tech Research Institute - Dr. Thomas Starr

Microstructural and structural characterization of ceramic matrix composites correlating mechanical properties to microstructural properties and to processing conditions.

14. Institute for Paper Chemistry

NBS researchers in the High Temperature Chemistry program have an ongoing interaction with the Institute for Paper Chemistry to develop a process model for the reprocessing of spent inorganic liquors in the production of paper. The institute is planning for Research Associates to work at NBS. NBS has provided the Institute for a preliminary computer model and thermodynamic data base to model the spent liquor reprocessing.

15. Max Planck Institut, Stuttgart, W. Germany

Joint work with Wolfgang Kaysser on sintering of ceramics and diffusion induced boundary migration in ceramics and metals.

16. Naval Research Laboratory

Cooperative research between R. P. Ingel of the Naval Research Laboratory and T. W. Coyle is performed concerning studies of transformation and toughening mechanisms in ZrO_2 containing ceramics.

17. Norton Co.

Cooperative research involving C. A. Willkens and N. Corbin of Norton Co. with T. W. Coyle has begun on the characterization of the mechanical performance of ceramic matrix fiber composites.

18. Oak Ridge National Laboratory - Drs. D. P. Stinton, T. M. Besmann and A. J. Caputo.

Microstructural and structural characterization of ceramic matrix composites correlating mechanical properties to microstructural properties and to processing conditions.

19. Stauffer Chemical Company

Chemists from Stauffer Chemical Company made an extended visit to Dr. J. J. Ritter of the Ceramic Chemistry Group to learn hands-on procedures for generating fine metal oxide powders from metal alkoxides. Both flask precipitation and flow-reactor precipitation techniques were addressed.

20. VAMAS

The Tribology Group are participating in the international wear test standardization project. Results of the first round-robin study have been submitted and recommendation for improved procedures are being prepared.

JOINT INDUSTRIES/UNIVERSITIES

1. AT&T Bell Laboratories, Trans Tech Division of Alpha Industries, University of Pennsylvania and Arizona State University

A joint program on dielectric ceramics having important microwave applications is being carried out by R. S. Roth, J. J. Ritter and J. Blendell in association with R. J. Cava, H. O'Bryan (Bell Labs), T. Negas (Alpha Industries), P. Davies (U. of Pennsylvania) using electron microscope facilities at NBS and Arizona State Univ. and with A. Olsen (Univ. of Oslo, Norway). Powders of barium poly-titanates (pure and doped) are synthesized from alkoxide precursors, conditioned, compacted and densified at NBS with phase equilibria and crystal chemistry determined at each processing step. Characterization of microwave properties (dielectric constant, Q, TCK, etc.,) is performed on NBS prepared powders and compacts by the

Industrial organizations. The University groups investigate the materials using high resolution electron microscopy lattice imaging techniques, correlating observed and calculated lattice image defects with the dielectric and thermodynamic properties. On the basis of collorative studies, the composition of the phase previously thought to be $Ba_2Nd_4Ti_{10}O_{28}$ has been shown to be $Ba_3Nd_4Ti_9O_{27}$ and a new product is being marketed with improved properties for microwave ceramic filter devices.

2. General Electric and Rice University

NBS participates in a joint program with NASA for materials processing in space. D. W. Bonnell (High Temperature Processes Group) plans, supervises, and participates in experiments jointly with personnel from GE and Rice University at the King of Prussia laboratory (PA). These experiments involve use of a state-of-the-art facility designed by Dr. Bonnell for levitation melting of tungsten and other refractory metals coupled with drop calorimetry. The results, in addition to providing basic thermodynamic information indicate the limitations of ground-based versus space experiments.

UNIVERSITIES

1 Alfred University

Materials for instrument line shape calibration in x-ray diffraction are being investigated jointly by C. Hubbard and R. Snyder (Alfred).

2. Johns Hopkins Unviversity

Robert Kelly of the Chemical Engineering Department and G. J. Olson and F. E. Brinckman are conducting joint research on microbial attachment to and solubilization of strategic metal ores characterized by non-destructive surface analysis techniques including epifluorescence microscopy and FTIR. Olson is guest lecturer in Chemical Engineering Department.

3. University of Alabama at Huntsville

A. Feldman and E. N. Farabaugh are collaborating with Dr. Karl Guenther of the University of Alabama in studying the relationship between processing, structure and properties of thin optical films. The research will aid in the development of optical films with increased stability and greater reproducibility.

4. Massachusetts Institute of Technology (MIT)

Joint work with R. Coble (MIT), C. Handwerker (Metallurgy Division), J. Blendell, K. Rhyne, and K. Frase (now at IBM's Watson Research Center), involves the characterization of flaws (pores) in alumina ceramics, by SANS and conventional microstructural techniques.

prepared at MIT and analyzed at NBS with the goal of correlating pore size distributions with SANS data; an important result will be the effect on pore size distribution caused by polishing and etching.

5. Northwestern University

Joint research involves lubrication modeling between S. Hsu and Prof. Herbert Cheng. The research focuses on the microelastohydrodynamic theories under wearing conditions. This is the first attempt at combining surface chemistry with surface mechanics to create a predictive wear model.

6. Pennsylvania State University

The Phase Diagrams for Ceramists Data Center has an ongoing contractual/collaborative interaction with K. Spear of the Materials Science Department. He is developing the mathematical basis and computer software for including NBS developed solution models into phase diagram optimization/prediction codes. At the present time, existing computer codes for phase diagram modeling, developed for relatively simple alloy and molten salt systems, are not applicable to the more complex ceramic systems, e.g., oxides. This technical advance is necessary to the successful implementation of the NBS/ACerS five year development program for a computerized ceramic phase diagram data base.

The Tribology Group has several joint research projects with the Department of Chemical Engineering and the Materials Research Laboratory at PSU. The principal collaborators are S. Hsu, R. Munro, and R. Gates of NBS and Prof. E. Klaus, Prof. L. Duda, Prof. S. Naidu, D. Deckman, and J. Yellets of PSU. The research projects include fundamental studies on the vapor phase lubrication of ceramic materials at high temperature; microstructural effects in ceramic wear processes; high temperature friction and wear tribometer design; and ceramic wear modeling which seeks to establish a theoretical understanding of ceramic wear processes.

7. Princeton University

A. Feldman is collaborating with Dr. Philippe Fauchet of Princeton University in measuring the phonon spectrum of thin optical films by means of Raman Spectroscopy. The experiments are expected to identify the crystalline and amorphous phases present in optical films, many of which are metastable. The research will aid in developing an understanding of the relationship between processing and structure which, in turn, will lead to more stable optical films.

8. Rensselaer Polytechnic Institute

G. J. Olson and F. E. Brinckman are collaborating with Professor Henry L. Ehrlich on mechanisms of silver ore solubilization and resistance in metal ore processing bacteria.

9. Rice University

D. W. Bonnell interacts with J. L. Margrave of the Chemistry Department at Rice University for the purpose of developing (and applying) state-of-the-art levitation calorimetric techniques. These techniques are needed for the determination of basic thermodynamic quantities of refractory materials (e.g., W, Ta, carbides) in their solid and liquid states. The collaborative effort is sponsored by the NASA Materials Processing in Space Program, and General Electric is a third member of this Government-University-Industry team.

10. Rutgers University

Joint work with J. Blum (Rutgers) and J. Blendell involves production of seeded sol-gel glasses to be used in studies of phase controlled crystallization at NBS.

11. University of California, Lawrence Livermore National Laboratory

Joint work with M. Weber (LLNL) and D. Blackburn and W. Haller involves the luminescent behavior of various elements in glass matrices. Matrix composition and processing conditions affect such parameters as emission wavelength, band width, life time and quantum yield which are of importance to glass lasers and optical frequency convertors. Oxide and non-iron-oxide glasses with emitting elements are developed at NBS and characterized for glass forming and element loading capability. LLNL measures optical parameters, and the results are correlated to glass composition. The goal of this work is to improve the understanding of luminescence and may lead to novel types of lasers.

In another joint work between NBS and LLNL, W. Haller collaborated with T. Bernat, D. Miller and other members of LLNL in the development of high pore volume aerogels. Aerogels of this type are used to study equation of state behavior under extreme conditions.

12. University of Cincinnati

Scientific collaboration with Prof. John S. Thayer on molecular mechanisms of metal solubilization and transformation by biogenic metabolites is being pursued.

13. University of Illinois

Steven Danyluk and Dae-Soon Lim of the Department of Civil Engineering, Mechanics, and Metallurgy are conducting joint research with S. M. Hsu and R. G. Munro of NBS. The project centers on an investigation of the fundamental mechanisms of friction, wear, and surface damage in tribological applications of advanced ceramics.

14. Drexel University

The Glass and Composite Group is conducting a joint program with Dr. M. J. Koczak of Drexel University on the fracture behavior of ceramic matrix composites.

15. University of Maryland

Members of the Surface Chemistry and Bioprocesses Group are collaborating with Prof. Michael Bellama and his doctoral students on biological and chemical transformations of organometallic materials in environmental situations. Brinckman is adjunct professor in the Chemistry Department.

C. Hubbard an A. Dragoo are participating in a collaboration with J. Stewart and Y. Zhang, of the University of Maryland, on the development of measurement an analysis methods for the determination o grain size and residual strain by x-ray diffraction. Samples of ultrafine grained MgO and ZrO_2 have been obtained. The study is expected to lead to a new Standard Reference Material.

16. University of Minnesota

Cooperative research is underway between S. Hsu and Prof. Ramalingam on ceramic coating and coating evaluation for advanced technological concepts.

17. University of New Hampshire

The Surface Chemistry and Bioprocesses Group is collaborating with Prof. Richard H. Blakemore on <u>in vivo</u> characterization of metal particle formation rates and sites in magnetite-depositing bacteria, using SANS characterization. G. J. Olson, F. E. Brinckman, and K. Rhyne are participating in the research.

18. University of Siena, Italy

G. J. Olson and F. E. Brinckman are collaborating with Dr. Franco Baldi on microbiological leaching of metal orea.

19. University of Southern California

B. Steiner and the Synchrotron Group of the Metallurgy Division have collaborated on monochromatic topographic examination of bismuth silicon oxide crystals during the first two weeks of dedicated x-ray ring operation at the National Synchrotron Light Source. These crystals display highly growth-dependent defects and strains associated with the detailed character of the crystal growth. Such defects can affect the performance of signal processing devices made from such crystals. Correlation of the topographic information with parametric variation in the crystal growth process will help to identify those aspects of growth that most critically affect device performance.

20. University of Tennessee Space Research Institute (UTSI)

UTSI functions are primarily of an industrial R & D nature. Their interaction with NBS has been long standing and revolves around their development of coal fired MHD systems and their need for NBS basic data and models of the MHD slag behavior. UTSI provides (E. Plante) with slag samples from their pilot plant tests, and NBS carries out basic vaporization and phase equilibria measurements on these samples. The results are used by UTSI and also by J. Hastie and D. Bonnell to develop predictive models of slag thermochemistry under actual MHD use conditions. NBS recently completed development of a highly successful model, which is now in use by Lloyd Crawford of UTSI. This model can predict the vaporization, seed retention, and phase equilibria behavior of complex MHD slags containing oxides of Na, K, Ca, Mg, Al, Si, and Fe.

21. Tsinghua University

Prof. Fu-Xing Wang is conducting research with S. M. Hsu and R. S. Gates of NBS concerning wear mechanisms of ceramic pairs.

22. State University of New York at Stony Brook: M.I.T.: U. of Maryland

P. Davidson couples her phase diagram modeling research with various university groups. These include, phase equilibrium experiments among olivine and pyroxene solid solutions in the CMFS system are being conducted in collaboration with D. H. Lindsley at S.U.N.Y.; a model for CMFS pyroxene crystallization from silicate liquids is being developed in collaboration with T. L. Grove at MIT; and modeling of crystal - liquid fractionation in basaltic liquids is being performed in collaboration with R. Nielsen at the University of Maryland.

23. Virginia Polytechnic Institute and State University

Cooperative research between Prof. Larry Taylor (VPI). P. Pei, and K. Jewett investigates surface reaction product analysis under wearing conditions.

24. Uppsala University

Prof. Olof Vingsbo is collaborating with S. M. Hsu in a project designed to identify the future critical issues in the tribology of ceramic materials.

STANDARD REFERENCE MATERIALS

The Division provided science, industries, and government a central source of well-characterized materials certified for chemical composition of physical or chemical properties. These materials are issued with a certificate and are used to calibrate instruments, to evaluate analytical methods, or to produce scientific data which can be referred to a common base.

DESCRIPTION	SRM NUMBER
Alumina Elasticity	718
Alumina Glass Anneal Point	714
Alumina Glass Anneal Point	715
Alumina Melting Point	742
Aluminum Magnetic Susceptibility	763-1
Aluminum Magnetic Susceptibility	763-2
Aluminum Magnetic Susceptibility	763-3
Barium Glass Anneal Point	713
Borosilicate Glass Composition	93(A)
Borosilicate Glass Thermal Expansion	731L1
Borosilicate Glass Thermal Expansion	731L2
Borosilicate Glass Thermal Expansion	731L3
Cadmium Vapor Pressure	746
Chrlorine in Base Oil	1818
Container Glass Composition	621
Container Glass Leaching	622
Container Glass Leaching	623
Copper Thermal Expansion	736L1
Fused Silica Thermal Expansion	739L1
Fused Silica Thermal Expansion	739L2
Fused Silica Thermal Expansion	739L3
Glass Dielectric Constant	774
Glass Electrical Resist	624
Glass Fluorescence Source	477
Glass Liquidus Temperature	773
Glass Refractive Index	1820
Glass Sand (High Iron)	81A
Glass Sand (Low Iron)	165A
Glass Stress Optical Coefficient	708
Glass Stress Optical Coefficient	709
Gold Vapor Pressure	745
High Boron Glass Viscosity	717
Intensity XRD Set	674
Lead Barium Glass Composition	89
Lead Glass Anneal Point	712
Lead Glass Viscosity	711

Liquids Refractive Index	1823
Low Boron Glass Composition	92
Lube Oil Oxidation Test Kit	1817
Lube Oxidation Catalysts	8500
Lubricant Oxidation Research Test Kit	8500a
MNF_2 Magnetic Susceptibility	766-1
Mica X-Ray Diffraction	675
Neutral Glass Anneal Point	716
Nickel Magnetic Susceptibility	772
Opal Glass Composition	91
Palladium Magnetic Susceptibility	765-1
Palladium Magnetic Susceptibility	765-2
Palladium Magnetic Susceptibility	765-3
Platinum Magnetic Susceptibility	764-1
Platinum Magnetic Susceptibility	764-2
Platinum Magnetic Susceptibility	764-3
Refractive Index Glass	1822
Respirable Quartz	1878
Ruby EPR Absorption	2601
Sapphire Thermal Expansion	732
Silicon X-Ray Diffraction	640(A)
Silver Vapor Pressure	748
Soda Lime Flat Glass Composition	S620
Soda Lime Float Composition	1830
Soda Lime Glass Viscosity	710
Soda Lime Sheet Composition	1831
Sulfur in Base Oil	1819
Toluene 5 ML	211C
Tungsten Thermal Expansion	737

APPENDIX

CERAMICS DIVISION ORGANIZATION

Division Office Telephone Number: 301-975-6119

Division Chief: Stephen M. Hsu

Division Staff: Mario Cellarosi
S. J. Dapkunas
Camden Hubbard

Properties and Performance Groups

Mechanical Properties
Sheldon Wiederhorn, 975-5772

Glass and Composites
Stephen Freiman, 975-5761

Tribology
Ronald Munro, 975-3671

Optical Materials
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Stanley Block, 975-5733

Ceramic Powder Characterization
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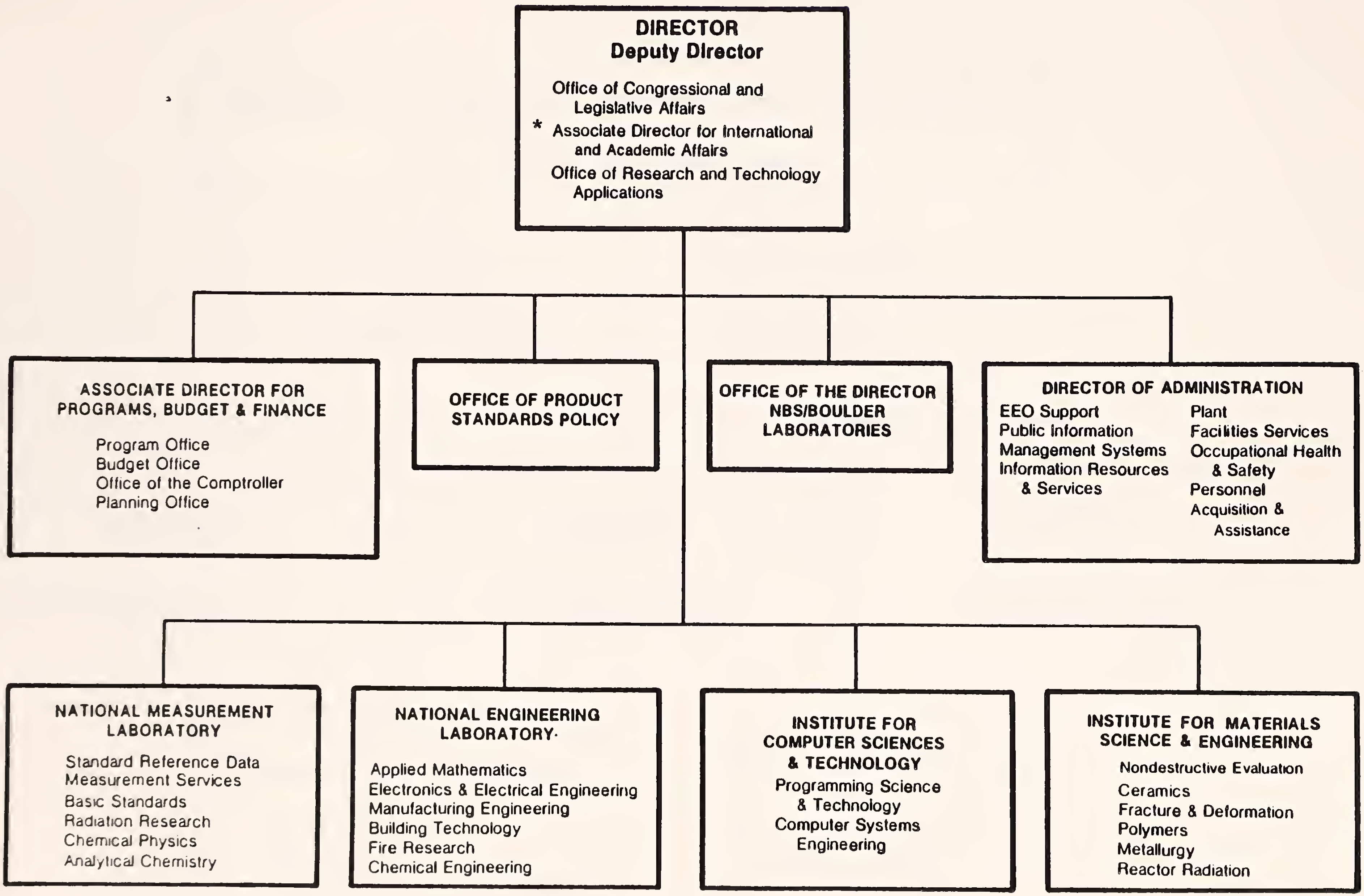

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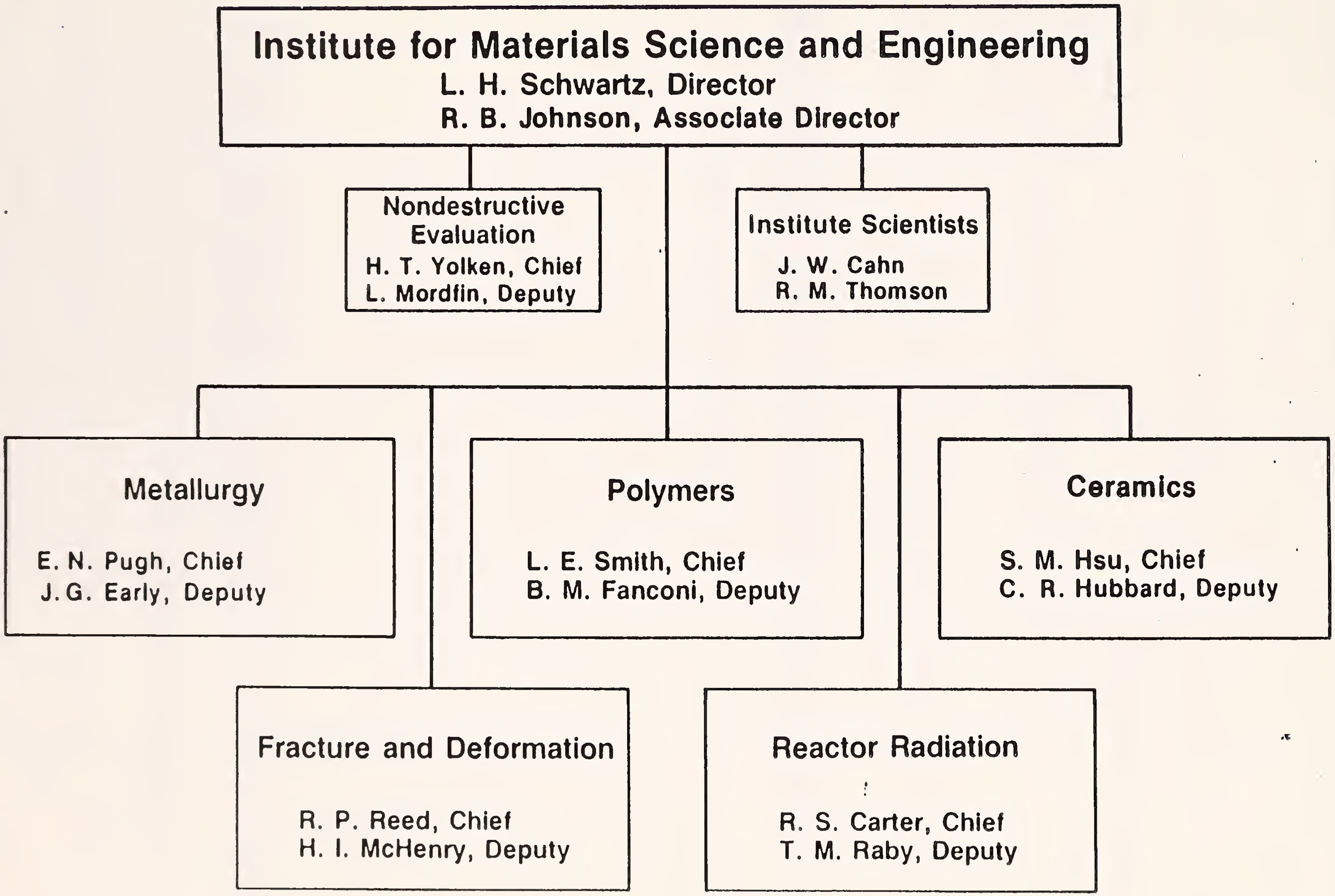
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Reactor Radiation
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NBS - Ceramics Division 420
Bldg. 223, Rm. A258
Gaithersburg, MD 20899

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

Current programs of Ceramics Division are reviewed.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

Composites; glass; mechanical properties; optical materials; powder characterization; thermodynamics; tribology.

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