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# CHEMICAL RESEARCH NEEDED TO IMPROVE HIGH-TEMPERATURE PROCESSING OF ADVANCED CERAMIC MATERIALS

## (Technical Report)

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†Professor Kolar died in February 2000 as this manuscript was about to go to press. It is dedicated in his honor by his colleagues on IUPAC Commission II.3 and the Inorganic Division. Final preparation of the manuscript was carried out by R. Metselaar, K. E. Spear, and G. M. Rosenblatt.

# Chemical research needed to improve high-temperature processing of advanced ceramic materials

*Abstract*: Of the principal classes of engineering materials, ceramics are in many ways the most interesting and challenging. Many properties, or combination, of properties, not achievable with other classes of materials give ceramics enormous technical potential. The main obstacles that prevent the wider use of ceramics include insufficient reliability, reproducibility, and high cost. The physical basis of the processing steps is well established, however, the chemical reactions which occur during the high-temperature processing frequently influence the densification process and microstructure development of ceramics in an unpredictable way. Therefore, an ability to understand and control the chemical processes that occur during ceramic processing are necessary to advance and open up new uses for technical ceramics. The aim of this present report, resulting from discussions of an *ad hoc* group of ceramists and chemists, is to expose the areas of chemical research that can most benefit the processing, and further the use, of ceramic materials.

## 1. INTRODUCTION

One of the major new directions in chemical sciences is devoted to advanced materials. Recognizing this development, the International Union of Pure and Applied Chemistry (IUPAC) is launching several actions to focus the attention of the chemical community on the important role played by chemists in the design and development of materials. One outcome of such an action is the recent monograph *Chemistry of Advanced Materials* edited by C. N. R. Rao in the IUPAC Chemistry for the 21st Century series [1]. This monograph is an excellent survey of chemical aspects of some important groups of materials. Another recent monograph reviewing political and educational aspects, together with selected research areas of materials chemistry, appeared recently as a volume of the Advances in Chemistry series [2].

Among the different classes of materials, advanced ceramics are a well-known group. The potential of advanced ceramics is reflected in a far-above-average rate of market growth, as shown in Table 1 [3]. Their performance in terms of electrical and magnetic properties, hardness, and heat, wear, and corrosion resistance, and the many possibilities of substituting them for strategic materials has attracted the attention of manufacturers and users for several decades, and thus has stimulated their rapid development.

Advanced ceramics do have well-known disadvantages. Desired parts are often difficult to fabricate reproducibly, and their properties may be strongly dependent on the purity and physical characteristics of the raw materials, and may be sensitive to small changes in processing parameters. They are often brittle, sensitive to microcracking, and difficult to machine. Continued growth in the use of advanced ceramics, therefore, depends on improving production quality and reproducibility, as well as the reliability of derived products. And, of course, cost effectiveness must always be retained.

Due to the importance of advanced materials in general, and advanced ceramics in particular, the potential and needs of these materials have been frequently reviewed. A number of governmental and professional society panels have been convened and the resulting reports published as recommendations [3–7]. All reports stress the importance of an interdisciplinary approach and call for better exchange of information among various experts involved in materials research and development.

**Table 1** World market[1] for new materials (billions of ECUs) [3].

| | 1986 | Average annual rate of growth, 1986–88 (%) |
|---|---|---|
| New iron and steel products | 50 | 2.3 |
| Engineering thermoplastics | 10 | 8.3 |
| Engineering thermosets | 15 | 5.5 |
| Nonferrous alloys and new metals | 13 | 3.8 |
| Composites | 12 | 8.7 |
| Structural ceramics | 7 | 13.9 |
| New glass-based products | 4 | 9.3 |
| Functional materials for electronics | 14 | 12 |
| Total | 125 | 6.4 |

[1] The United States, Japan, and the 12-Member EEC aggregated. Source: BIPE, Observatoire des materiaux nouveaux, 1988 (ECU = 1.1 $, 1988).

While the need for interdisciplinary research in materials science and development of metals, polymers, and ceramics is well recognized, ceramics requires the most interdisciplinary approach of these three classes of materials. This requirement is related to the fact that ceramics and glasses have an enormous range of structures, properties, and applications. As an example of the required interdisciplinary approach, the recent discovery of ceramic superconductors attracted not only ceramists, but physicists, preparative chemists, crystallographers, chemical technologists, electronic and mechanical engineers, and many others. However, many highly qualified but narrow specialists working alone or in small specialized teams soon became frustrated by the complexity of the subject. After the initial euphoria, only well-trained and well-equipped interdisciplinary teams have remained to develop the immense potential of ceramic superconductors into practical devices.

It is the strong belief in the ceramics community that the great potential of advanced ceramics can be exploited further and faster only when the unsolved problems in the circle of "synthesis–processing–microstructure–properties" are made widely known to the various specialists who can contribute to their interdisciplinary solution. These specialists include chemists, who can contribute to the development of ceramics particularly in the areas of the synthesis, structure, properties, and chemical reactivity of these materials.

The aim of the present review is to outline some emerging problems in ceramic processing that are closely related to the chemistry of the systems. The review is limited to polycrystalline bulk ceramics, which, by far, represent the largest market segment of the ceramics industry. Most of the topics discussed concern the central processing step in ceramic production, the high-temperature treatment. Specific problems of new emerging technologies and products, such as fibers and composites or ceramic coatings, are not covered. It is true, however, that numerous basic problems in bulk ceramic processing are also important for these new and emerging technologies. Monocrystals are also not considered. The chemical synthesis of powders is not extensively discussed because of several recent comprehensive reviews and conference proceedings (see references in Section 3 of this article).

## 2. COMPLEXITY AND CRITICAL ISSUES IN CERAMIC PROCESSING

The most common criticism of those who wish to exploit the potential of ceramics and of those involved in its production is that ceramic parts often fail to meet their expected performance levels. The major and overriding problem of high-performance ceramics is that components with the desired properties cannot be reliably and reproducibly manufactured and offered on the market at acceptable prices [6]. It is believed that this is so primarily because the basic science and understanding are not available to support the fabrication technologies, and, thus, the desired densities and microstructures cannot be reproducibly obtained.

The major drawback in large-scale ceramic production is the lack of reproducibility, which is largely due to large changes in the microstructure that can occur with small changes in composition and/or processing parameters. The relationship of microstructure/processing parameter changes is typically nonlinear. It must be also recognized that different applications may require different properties/microstructures, even for the same material. Achieving acceptable mechanical properties of ceramics, such as toughness or brittleness, is often a major problem, limited by the worst flaw in the fabricated part. Optical properties controlled by light scattering require the absence of second phases and pores. The optimum microstructure for dielectric ceramics depends on the specific application. In some cases, the grain boundary phase may limit conductivity and in other cases, this limited conductivity may be an asset.

Chemistry plays a key role in the research and development of ceramic processing. This fact is reflected in recent introductory ceramic textbooks, such as *The Chemistry of Ceramics* by Yanagida, Koumoto, and Miyayama [8] and *Physical Ceramics* by Chiang, Birnie, and Kingery [9]. Both textbooks heavily rely on the subjects of solid state chemistry, crystallography, inorganic chemistry, chemical thermodynamics, and kinetics as applied to ceramics materials. For chemists involved in ceramics research and technology, but without previous special training in ceramics, familiarity with such textbooks is obligatory.

The words “synthesis” and “processing” may have different meanings to different professionals. To chemists, synthesis typically means the act of making the required material. To ceramists, synthesis and processing are often used interchangeably to mean preparing a ceramic material. This usage may imply not only making the material, but also making it in a desired form such as a specific size/shape of powder, a crystalline or amorphous coating/film, or bulk single or polycrystalline material. Ceramic material preparation is usually referred to as “ceramic synthesis and processing”, or more frequently “ceramic processing”. In this review, we used the term processing.

The words “fabrication” or “production” are less appropriate for this review because they stress the industrial operations of producing a ceramic part in a form or shape suitable for a given application.

Another word that can have different meanings for chemists and ceramists is “structure”. In solid-state chemistry structure implies a crystal structure. In ceramics, structure covers a wide range of structures, ranging from arrangement of atoms to assemblies of crystalline grains that may have sizes ranging from submicrometers to millimeters. Assemblies of crystalline grains are typically referred to by the expression “microstructure”. In a microstructure, ceramists must distinguish between the structure of the grains that are regarded as minute monocrystals, and the structure between the ceramic grains and their surroundings (i.e., grain boundaries). The grains may be all of one phase (compound), or may be a mixture of two or more phases. Thus, the “polycrystalline material” may be “single phase” or “multiphase” in composition.

Standard powder processing steps in making ceramic articles are well described in ceramic textbooks. In short, ceramic processing involves preparation or synthesis of raw materials or starting compounds in powder form, forming the powder into a bulk shape (the shape may range from a pellet to a piece to be used in an application), high-temperature treatment (termed “sintering”), and a final finishing step if an application is involved.

The forming of a ceramic article from powder results in a porous compact. During sintering the constituent ions or atoms have a driving force to redistribute themselves so as to minimize the Gibbs energy of the system. The ions or atoms are transported from the interior of the grains along the grain boundaries to adjacent pores that are eventually filled. This action converts a compacted powder into a denser structure of crystallites joined to one another by grain boundaries.

Most ionic ceramic powders readily undergo densification up to ~95% of theoretical density if the particle sizes are sufficiently small. In contrast, covalently bonded materials such as $Si_3N_4$ or SiC, because of low diffusion coefficients of transporting species, usually need additives that serve as sintering aids to enhance densification.

Increasing the surface area of starting powders increases the rate of densification or sintering. The finer particle size results in a higher surface energy for a compact, and thus a higher driving force for grain growth (growth of crystallites) and densification to reduce the system's Gibbs energy. Larger crystallites and a decrease in porosity both result in a decreasing surface area, which decreases the Gibbs energy of the compact. If crystal growth is too rapid, pores may be detached from the grain boundaries and stabilized in the interior of the grains. Eliminating such porosity is difficult and can limit the extent of densification. Increasing the sintering temperature increases the rate of diffusion, which can increase the rates of grain growth and densification. The vast majority of useful ceramics are multicomponent and multiphase. Most frequently, the densification is accelerated by the presence of a small amount of material that forms a liquid phase at the sintering temperature, and exhibits a limited solubility of the primary phase (compound) in the compact.

High-sintered density is not necessarily always the aim in ceramic processing. Ceramics with purposely created, but controlled porosity may have important applications, for example, as gas sensors or thermostable ceramic membranes.

Ceramic membranes 1–5 μm thick with pores of 2–50 nm have been developed for microfiltration and ultrafiltration applications, for example the treatment of oil–water and oil–latex emulsions in waste water, the recovery of textile sizing agents, the extraction of proteins from whey, the classification of beverages, and a number of biotechnological applications. High-temperature applications include the processing of high-molecular-weight mixtures in the petrochemical industry [106].

In making ceramic membranes, special techniques have been developed to assure that sufficient mechanical strength is obtained. The main process includes preparation of a dispersion of fine particles and deposition on a porous support by slip casting or film coating. The most critical step in the preparation of membranes with controlled nanoporosity is drying and calcination, which should be regulated to avoid cracking and pore closure. Important controlling parameters are slip characteristics (particle shape and concentration, agglomeration degree, binders, or plasticizers) and roughness and pore size of the support. As in the case of sintering to high density, understanding and tailoring the mass transport mechanism during high-temperature treatment is of paramount importance also in the preparation of porous ceramics.

In 1978, Coble and Cannon [10] delineated a framework for understanding powder processing of ceramics: "to connect the behavior and changes in the behavior of ceramics to controllable variables and operations: empirically, by measurements; and fundamentally, by theories and models and the material properties database".

Controllable variables and operations are:

- powder preparation
- dopant/impurity distribution
- shaping
- firing (heat treatment cycle of heating up, holding at temperature, cooling)
- pressure (when applied during firing)
- vapor pressures of gaseous species

Parameters, which appear in expressions used in a theoretical model for describing shrinkage, densification, and grain growth during the sintering process are listed in Table 2.

Included are:

- Surface energies: solid/vapor $\gamma_{s,vap}$, liquid/vapor $\gamma_{l,vap}$, solid/liquid $\gamma_{s,l}$, solid/solid $\gamma_{s,s}$ and, more generally, grain boundary or interphase energies $\gamma_b$ with composition (impurities and dopants $i$, with concentrations $X_i$) and temperature dependencies.

- Diffusion coefficients: Lattice $D_{lat}$, boundary $D_b$, Surface $D_{surf}$, $D$'s in molten phase (when present). Diffusion coefficients of both cations ($D^m$) and anions ($D^x$) ought to be documented or predictable. Again, values for pure and doped or impure materials (intrinsic and extrinsic) and their temperature dependencies are needed.
- Reaction rate coefficients: bulk ($k_n$), interphase ($k_b$) with composition dependencies
- Vapor pressures for cation and anion species ($p^m$, $p^x$)
- Viscosity and wettability in presence of liquid phase

It is a general belief among ceramists that the theoretical understanding of sintering and grain growth processes is well enough advanced to be used in a predictive mode when enough other background data are available. Theory offers a firm background to design the processing parameters in the development and manufacture of ceramic products. The limited database is a greater handicap than the modeling. More data are needed on the impurity effects or dopant effects on surface energy, the grain

**Table 2** Sintering and hot pressing with/without liquid in metallic, ionic, or covalent systems [10].

| *Behavior* | *Controllable variables and operations* | *Database needed** |
|---|---|---|
| General morphology | Powder preparation, particle size | $\gamma_{s,vap}$, $\gamma_{l,vap}$, $\gamma_{s,l}$, |
| Evolution of pores and grains | Particle shape, distribution | $\gamma_b = f(X_{dop\ i}, X_{imp\ j}, ...)$ |
| Density $f(T,t)$ | Dopant distribution | |
| Grain size $f(T,t)$ | 2nd phase distribution | $D_{lat}^m$ $D_{lat}^x$ |
| Dopant effects | Fabrication | |
| | Density distribution | $D_b^m$ $D_b^x$ |
| | Pore size " | |
| | Firing | $D_s^m$ $D_s^x$ |
| *Models* | $T$ and $T_{max}$ | $D$'s in liquids |
| | $p(t)$ | |
| Neck growth | $p_g$, atmosphere | $k_n^{m,x}$ $k_b^{m,x}$ |
| Surface area change | | $p^m$ $p^x$ |
| Shrinkage | | |
| Densification in later stages | *Characterization Measurements* | |
| Defect reactions at surfaces | | Phase equilibria |
| | | Gas solubilities |
| Diffusive transport | Shrinkage, density | Diffusivities |
| Evaporation condensation | Neck growth | Solute diffusivities |
| | Surface area change | Creep behavior |
| Plastic flow | Grain size, pore size, and continuity | $y = f(T)$ |
| Gas pressure effects | | |
| Grain growth | Permeability | |
| Solute drag | Strength | |
| Pore drag | Conductivity | |
| Pore breakaway | Porosimetry | |
| | Dopant redistribution | |
| | $f(T,t)$ | |

*Terms are defined in text.

boundary energy, interphase energy, surface diffusion coefficients, boundary and lattice diffusion coefficients, all as a function of dopants, for a range of specific systems of interest [10].

It must be emphasized that many of these parameters are interrelated. For example, the same type of microstructure may be realized for various starting powders by varying the processing [11]. One can envisage two ideal situations: (i) the availability of perfect powder, robust enough that it will not require careful processing, or (ii) fixing all problems with imperfect powders by adjusting the process parameters.

In chemically non-equilibrated compacts, chemical reactions between different constituents in the ceramic body and between the sintering atmosphere and the ceramic take place simultaneously during the sintering process. Chemical reactions that take place by interdiffusion of constituent ions or by a dissolution/precipitation process in presence of a reactive liquid greatly influence the densification and microstructure development during the sintering step.

## 3. CONTRIBUTION OF CHEMISTS IN CERAMIC PROCESSING

Synthesis of new compounds is a prime occupation of a large number of well-qualified and experienced chemists throughout the world. However, synthesizing new compounds with prescribed properties, needed for the manufacture of ceramics for a particular application, is a much more difficult task than the mere synthesis of new compounds. The knowledge base of basic principles, which would guide the professional to synthesize compounds with a desired combination of properties (for example, high-dielectric constant/high-temperature stability of the dielectric constant), is limited. Usually one strives toward incremental improvements of properties by modifying the composition of known compounds, which were found by chance to possess the useful combination of properties. Muller and Roy recommended systematic, science-based guidelines that one should follow in search for new compounds with particular properties, and they illustrated the approach with several examples [12]. In this respect, the classification of groups of compounds with particular crystal structures, according to the constituent ionic radii ("structure field maps") is of particular value [13,14].

Availability of compounds with a useful set of properties is the starting point in preparation of ceramics. To realize the potential of the compounds, appropriate technologies for making ceramics with optimal properties must be developed. Important is the knowledge that, in many cases, useful properties of a particular compound may be exploited only after processing the material into a polycrystalline ceramic. Examples are functional ceramics based on grain boundary phenomena or heterogeneous microstructures.

The usefulness of a ceramic depends on two factors: the availability of compounds with specific desired properties, and appropriate technologies for making ceramics with optimized properties. Frequently, the two activities cannot be separated due to the fact that the main processing step in ceramic technology subjects a material to a high-temperature treatment, which simultaneously greatly increases the reactivity of solids.

The synthesis of new compounds and the determination of their basic characteristics, such as crystal structure and thermal stability data, are not enough to draw the attention of ceramists. What is needed is an evaluation of electrical, magnetic, optical, mechanical, thermal, and other properties [15]. Fortunately, this aspect of synthesis is being increasingly recognized, as demonstrated in current articles in professional journals and proceedings. Success has been achieved by expanding the synthetic groups to include the physical measurements or by close cooperation of various groups.

One of the most important contributions that chemists can make to improve high-temperature processing of advanced ceramics is to provide chemical means to improve homogeneity and reproducibility of "green" (i.e., unfired) ceramic parts, such that the sintering process can take place at lower temperature and can result in less residual porosity, possibly smaller grains, and a more homogeneous microstructure. This is actually a low-temperature activity, whose result is referred to in ceramic fabrication by a specific term, “sinter-active” powders. Such “active” powders can have a dramatic effect on high-temperature processing.

The traditional ceramic method for the preparation of a compound involves mixing and grinding various starting powders and heating them at high temperatures, with intermediate grinding when necessary.

The trend today is to avoid such a brute force method to obtain better control of crystal structure, stoichiometry, purity, and morphology. In the last 15–20 years, the chemists have shown increasing interest in the chemical preparation of compounds in powdered forms for ceramic processing. In addition to higher purity due to the avoidance of a milling operation, chemical methods yield, if optimized, narrower particle size distribution with less aggregation and agglomeration. The ultimate goal is homogeneous, dense, single-phase particles.

New, widely investigated methods of chemical synthesis include coprecipitation, the use of molten salts, sol-gel processes, hydrothermal techniques, liquid-phase and gas-phase reactions, polymer pyrolysis, aerosols, emulsions, and others. An excellent review was published recently [103].

The problem that needs even more attention when employing chemically prepared powders is the shaping process in making ceramic parts. Powder suspensions are inherently proper for shaping of articles by casting, however better control of colloid chemistry during consolidation from suspensions is needed, such that a homogeneous random packing is achieved without extended spatial correlations between pore positions. The latter leads to flaw formation and pore growth during sintering. To achieve this goal becomes increasingly difficult with decreasing particle sizes. Nanoscale particle size dimensions become equal to the double-layer thickness and the dimensions of sterically stabilizing molecules.

Subjects that need to be examined are:

- Double-layer stabilization of microscale particles
- Steric stabilization, especially for dual phase mixtures
- Adsorption stabilization for nanoscale particles; this method may yield a very small dimension (1 nm) of the stabilizing layer.
- Micellar and micro emulsion techniques to obtain high-density nanoscale particle packings
- Colloidal phase diagrams
- Advanced characterization of (green) porous structures
- Long-range solid-solid interactions in liquid media
- Further development of colloidal consolidation methods such as slip-casting, gel-casting, colloidal filtration, centrifugal consolidation, and electrophoretic deposition
- Better understanding of the rheology of coating processes
- Better understanding of drying processes and the role of drying control

Chemical methods are attractive for ceramic processing because some of them allow direct fabrication of coatings, fibers, and monoliths without powder intermediates. Examples include controlled-porosity coatings for ceramic membranes, coatings on window glass for selective transmission and reflection of solar radiation, optical fibers, and fibers for low weight, high-temperature stable thermal insulation, electroactive thin and thick films, and others.

The increased interest in the chemical synthesis of ceramic powders is illustrated by the vast number of publications in periodicals and proceedings of specialized conferences, such as Materials Research Society’s “Better Ceramics Through Chemistry” [16–22], American Ceramic Society’s symposia [23–26] and other publications [27–31]. While earlier conferences on ceramic processing science and technology focused only on powder processing, the conference in Friedrichshafen in 1994 covered the entire spectrum of ceramic processing [26].

In recent decades, researchers were notably successful in improving the quality of ceramic powders by modifications of existing processes, and in developing novel powder preparation techniques to prepare homogeneous, fine grain size, non-agglomerated, and sinter-active powders. However, the availability of dependable, accurate, and cost-effective powder characterization methods is still quite limited. Ceramists responsible for production usually obtain sparse information from suppliers of powders about their products' overall chemical purity, list of main impurities, and average agglomerate size with upper and lower 10% of size range. In the absence of detailed characterization information, ceramists in production must rely on their own experiments to check the sinterability of powders and the expected properties of the sintered products.

The variable characteristics of successive powder batches and the inadequate characterization of powders are important causes for the nonreproducible processing of ceramic parts. Table 3 lists the characteristics of powders for advanced ceramics that influence the processing and properties of ceramic products [32,33]. Ceramists are faced with the question of what characteristics of powders are most important and are to be measured for a given process. Clearly economical, fast, and reliable methods of powder characterization are very much in demand.

Other aspects of chemical research related to ceramic processing in addition to chemical synthesis have attracted less attention from chemists in the past. Chemists specialized in solid-state and high-

**Table 3** Powder characteristics that influence ceramic properties and forming processes [32,33].

*Forming process-oriented:*

Specific surface area
Primary particle size and size distribution
Agglomeration/aggregation
Agglomerate size and size distribution
Porosity, total and pore size distribution
Density
Sinter activity

*Property-oriented*

a) Bulk

Phase composition
Crystalline phases, quantity and identification
Amorphous material, quantity
Chemical composition
Stoichiometry
Major element concentration
Minor impurities (10 ppm to <1%)
Trace impurities (10 ppm)
Inorganic elements
Organic elements
Composition of impurities
Homogeneity

b) Surface

Major elements
Minor elements
Trace elements
Inorganic species
Organic species

temperature chemistry seem to lack an awareness of problems in ceramic processing. And yet it is the high-temperature treatment that decisively influences the microstructure properties and performance of ceramics.

## 4. PROBLEMS IN CERAMIC PROCESSING

### 4.1. Chemical heterogeneity

To improve the performance of ceramic products, and to increase the reliability and reproducibility in the manufacturing process, the producer has to decide between two concepts. Harmer described the concepts by using a well-chosen parable, "curing the disease" and "infallible" approach [11]. In the first approach, the producer accepts the fact that the raw materials and ceramic process give rise to several faults which, without proper countermeasures, limit the quality of the products and decrease the yield. Such faults are, for example, pore breakaway from moving grain boundaries during the sintering process, or exaggerated grain growth. "Proper countermeasures" are most frequently the sintering aids, that is, the additives that essentially decrease the influence of small variations in impurity content, powder morphology, or processing parameters on the properties of the finished product. As an example, in the production of $Al_2O_3$ ceramics, it was found that minute amounts of MgO improve the immunity of these materials from the described faults.

The problem of this "medical" approach is that there is no universal "remedy", for example, that the specific additives have to be found for each system in production. Such an empirical approach is time-consuming and expensive. Fortunately, accumulated knowledge based on experience, theoretical analysis, and systematic basic research has provided a general fundamental understanding of the role of additives in powder processing, and a rational choice of additives for various systems. Supporters of this approach firmly believe that an additive cure will be found for the majority of host systems.

The second approach is based on the fact that the finding of proper additives and processing parameters as countermeasures for faults in raw materials and the manufacturing process is a slow and complex process, demanding extensive fundamental and applied research. The number of systems for which the influence of additives is understood well enough to enable rational choice is limited. Thus, the second approach, the "infallible" one, relies on the use of the purest and morphologically most suitable raw materials (small particle size, equiaxed shapes, narrow size distribution, uniform non-agglomerated powders) and on optimized processing (dense, uniform green bodies, optimal firing conditions). This "infallible" approach always yields good results after firing. The problem with this approach is that it is expensive, demands sophisticated equipment, and is more restrictive in the products that can be fabricated.

The vast majority of producers—with rare exceptions of those which supply the strategic ceramic products where the price is not a restrictive item—rely on the first concept and incorporate additives into their formulations. Since additives at sintering temperatures react with basic components of the product, ceramic production is chemically controlled.

### 4.2. Chemical reactions in high-temperature sintering processes

The sintering process is, from a chemical point of view, most frequently a "reactive" or "reaction" process. In the ceramic literature, the term "reactive sintering" is typically used only when one wants to stress that the chemical reaction accompanies densification during firing [34–36]. The extreme case is represented by "chemical reaction forming". This technique, also known as "reaction bonding", is regarded as a technically important alternative route to conventional ceramic processing. The advantages are low processing temperatures, low raw materials cost, near-net-shape tailorability, and glass-phase free grain boundaries. Especially the low-to-zero shrinkage capability makes most reaction forming techniques suitable for making composites. Important examples of materials manufactured by employing the chemical reactions are reaction bonded-silicon nitride (RBSN), reaction-bonded silicon carbide (RBSC), and reaction-bonded aluminum oxide ceramics (RBAO).

RBAO objects are manufactured by heat treating in air the attrition-milled $Al_2O_3$/Al compacts, so that the Al metal particles are oxidized to small “new” $Al_2O_3$ crystallites which sinter and thereby bond the larger “old” $Al_2O_3$ particles [37]. Low-shrinkage monolithic $Al_2O_3$ ceramics are readily fabricated, since the 28% volume expansion associated with the Al to $Al_2O_3$ reaction partially compensates for shrinkage on sintering. The RBAO process can be modified in various ways by incorporating metal and ceramic additives to change the final alloy composition, to accelerate the reaction, and to further compensate for the sintering shrinkage. Most RBAO- and RBAO-based materials thus contain $ZrO_2$ known to hinder grain growth in $Al_2O_3$ [38] and to improve the mechanical properties [39].

The high potential of reaction forming may be exploited fully only if chemical reactions and processing parameters are carefully controlled. Problems frequently encountered are cracking, bloating, and poor reaction behavior. Important parameters controlling the manufacturing process are reactive metal content, particle size, and green density. Successful fabrication of high-strength bodies requires fine and homogeneous powders. Low milling intensity does not lead to the required particle fineness, whereas over-milling causes extensive oxidation. Fine metallic particles may contain physically adsorbed and chemically bonded water, which promotes cracking on heating. If the surface region becomes dense before complete decomposition of hydroxides in the interior of the object, bloating occurs.

Chemical reactions can be utilized also in forming green ceramic bodies. An example is the hydrolysis-assisted solidification (HAS) process, based on thermally activated hydrolysis of aluminium nitride powder added to highly loaded ceramic suspensions [105]. During hydrolysis of AlN water is consumed and ammonia is formed, which in turn may increase the pH of the suspension. Both mechanisms can be used to increase the viscosity and ultimately to set a cast or injection-molded ceramic green body. By using the HAS process, high green and sintered densities were obtained with alumina and Yttria Tetragonal Zirconia Polycrystalline material (YTZP), indicating the potential of this forming concept for the near-net-shaping of various high-performance ceramics.

The term “reactive sintering” is further used in ceramic processing to expose the particular influence of chemical reactions on the formation of ceramic products. A reaction in this sense may be the formation of the intended product [40–43]. However, the term is also used when oxidation–reduction reactions [42], phase transitions [44], or the formation of a solid solution [45] or a liquid phase [46,47] are involved.

The general principles of reaction sintering have been outlined by Yangyun and Brook [35]. Depending on the material and processing variables, such as powder particle size, sintering temperature, and applied pressure, reaction and densification can occur in sequence, concurrently, or in some combination. It is important to understand how these process variables influence the rates of reaction and densification to achieve adequate control of the fabricated microstructure. In reaction sintering, some variables which are not very critical in the sintering of chemically homogeneous, pre-reacted powders, such as heating rate, are much more critical and may be used as an effective variable for manipulating the rates of densification and reaction [48].

When there is a chemical reaction occurring during sintering, the occurrence of diffusion-induced grain-boundary migration (DIGM), also known as chemically induced grain-boundary migration (CIGM), can cause changes in the microstructure and kinetics of densification. For an extensive review, see [104].

DIGM causes otherwise stable grain boundaries to migrate, often increasing their area, and leads to much higher rates of reaction, or mixing, than would be achieved without the moving grain-boundary. Also, the migration can lead to wavy boundaries and, if extensive, to grain size reductions rather than grain growth as is normal.

The presently accepted explanation of the DIGM is that when solute diffuses down a grain boundary or an interface between two grains, there is lattice diffusion into the adjacent grains. This diffusion creates a strained layer as, except for very special compositional changes, any change in composition is accompanied by a change in lattice parameter. The layer is coherent with the bulk material, which has the original lattice parameter, and thus the layer is strained. This strained layer need only be one atom layer thick. The stress difference across the boundary will induce it to migrate. As long as diffusion ahead of the boundary is fast enough the boundary will continue to move, and solute that is diffusing down the boundary will be left behind in the region swept out by the boundary. Since the initiation and migration are not necessarily uniform along the boundary (due to variations in boundary direction, strain relief due to dislocations, and other non-ideal aspects of the interface), the migration is usually irregular along the boundary and unpredictable.

While the physics of DIGM is well understood, the effect on sintering has not been investigated in detail. It is thought that the effect may be large in certain reactive systems at relatively low temperatures when grain-boundary diffusion dominates.

In view of the reported observations on the prevailing influence of chemical reactions on the kinetics of densification and microstructure development, it is surprising that ceramists often neglect the reactions caused by impurities and additives, which are often included in the “simple” sintering process.

Yet it was pointed out that ceramics produced under standard laboratory conditions contain at least 1000s of ppm impurities due to both the impurity concentrations in the starting materials and from contamination of materials during processing and firing [49]. It is realized today that many ceramics earlier thought to be single-phase bodies in fact contain liquids at the sintering temperature due to impurities [50–57]. For example, abnormal grain growth in undoped $Al_2O_3$ [54] and $Fe_2O_3$ [51] is ascribed to unintentional silicate-based liquid phases. In short, most sintering processes may be regarded as reactive sintering. It is clear that possible high-temperature chemical reactions must be considered in all sintering processes.

Two conclusions may be formulated:

a) There is a need for new economical chemical methods for the preparation of large quantities of sinter-active powders with acceptable purity. “Acceptable” purity does not necessarily means the highest purity obtainable. Controlled and (within certain limits) reproducible concentration levels of impurities will lead to lower variability in final properties. Actually, it has to be proven that higher purity will improve properties. High purity may easily make properties more variable due to the large effect of small changes (i.e. due to the nonlinear response of properties upon impurity concentrations).

b) Despite the advances in synthetic methods, the “ceramic” method of ceramic processing (calcining and milling) remains for the time being the mainstay for ceramists, and even for solid-state chemists. In such cases, knowledge of the impurity content is not enough. The chemical reactions that take place among the impurities and host material in each system at high temperatures must be studied, and their influence on densification, microstructure development, and the properties of ceramics ascertained.

Besides impurities, additives purposely introduced to control the densification, grain growth, and properties of the ceramic articles influence the processing and properties of ceramics. This is explained in more detail in the following paragraphs.

### 4.3. Influence of additives on sintering and microstructure of ceramics

Yan [58] presented a list of possible dopant effects on microstructural development (Table 4). In an extensive review, the author supports the list by numerous examples from the published literature.

It is difficult to generalize about the influence of additives. Brook listed several reasons [59]:

- Additives and impurities, even at low concentration levels, can influence many factors such as interfacial energies, diffusion coefficients, grain-boundary mobility, and grain-boundary phase distribution.

**Table 4** A list of possible dopant effects on microstructural development [58].

(A) *Effects of solid solution*

(1) Changes defect concentration and diffusivities
(2) Causes solute drag on grain boundary motion
(3) Changes $\gamma_b/\gamma_s$ ratio
(4) Promotes grain growth

(B) *Effects of second phase*

(5) Provides high diffusivity paths
(6) Causes pinning on grain boundaries
(7) Promotes densification by solid second phase

- A great complexity of detail can arise in any of these interactions.
- Impurities, even at low concentration, can have a major influence on such factors.

For example, the ability of a small amount of MgO to prevent nonuniform grain growth and improve the sintering of $Al_2O_3$ is considered to be very specific. The phenomenon is not applicable to other systems. It is a general view that each individual system must be studied thoroughly to obtain a true and full picture of a particular interaction. It is hoped that comparison of data from many different systems will eventually establish a basis for composing a general picture of the significance of a given additive property.

Concentrated investigations of a limited number of systems have already generated not only specific data needed to optimize the processing of specific types of ceramics, but have also yielded general principles applicable to other systems. Such is the case for $Si_3N_4$-based engineering ceramics, which is described more in detail below.

### 4.4. Sintering chemistry of additives in bulk nitride ceramics

The complex role of additives and chemical reactions during sintering of advanced ceramics may be illustrated with silicon nitride ceramics. These additives play a role in controlling phase formation, microstructure, and properties of the bulk ceramics. Intensive investigations in many laboratories have led to improved knowledge of the basic relationships among processing, microstructure, and properties of these materials, and the results have been published in several conference proceedings [60–62].

Of all types of engineering ceramics, silicon nitride and its solid solutions with aluminium oxide (sialons) have probably the most useful combination of engineering properties, as well as flexibility in manufacture. Single-phase $Si_3N_4$ has a number of outstanding engineering properties: high strength, high fracture toughness, thermal stability to ~1850 °C, good oxidation resistance, low coefficient of thermal expansion and consequently good thermal shock resistance, and a modulus of elasticity greater than many metals. For manufacturing reliability, high-performance engineering $Si_3N_4$ components had two demanding problems that had to be solved: (a) sintering to high density and (b) the development of an optimized microstructure.

Silicon nitride is intrinsically difficult to sinter because of its basically covalent bonding and low self-diffusion coefficient. Densification is achieved by liquid-phase sintering. Following the early identification of effective sintering additives [63] and a recognition of the microstructure development mechanism as a solution-reprecipitation process within a silicate-based liquid [64], the subsequent development of sintering additives has proceeded largely through empirical studies. Common additives are MgO, $Y_2O_3$, $Al_2O_3$, and rare earth oxides. The oxides react with $SiO_2$, which is always present on the surface of $Si_3N_4$ particles, to form an oxide melt and at higher temperatures an oxide-nitride melt by dissolution of $Si_3N_4$.

The additive content required for complete densification depends on the sintering techniques. 2–5 vol % additives are sufficient if densification is helped by a high external pressure, (i.e., by hot pressing or hot isostatic pressing). Pressureless sintered materials usually require an amount of additives up to 15 vol %.

The microstructure that develops during liquid-phase sintering consists of elongated $Si_3N_4$ needles embedded in a matrix of smaller equiaxed $Si_3N_4$ grains and a grain-boundary phase. A typical microstructure, taken from ref. 93, is shown in Fig. 1. Considerable research has been conducted to improve the mechanical properties of silicon nitride through an understanding of the relationship of microstructure to mechanical properties, and of the processing required to develop desired microstructures [65–67].

Optimal microstructure depends on property requirements. Most researchers agree that coarse microstructures with elongated grains induce increased fracture toughness, possibly due to enhanced crack deflection and crack bridging [68,69]. Li and Yamanis [70] reported that $Si_3N_4$ ceramics containing large (≥ 1 μm diameter) elongated grains could exhibit fracture toughness up to 10 MPa $m^{1/2}$. However, the fracture strength of such ceramics (800–900 MPa) is considerably lower than that of materials with fine-grained microstructures, which can achieve exceptionally high fracture strengths of 1000–1500 MPa with lower fracture toughness [71].

Substantial published data [72–74] have shown that the properties of silicon nitride ceramics are, to a large extent, controlled by the type and quantity of the intergranular second phase. Liquids used to assist sintering of $Si_3N_4$ generally completely wet the $Si_3N_4$ grains. The fracture strength depends on the interface strength; a weak interface is required to induce transgranular fracture. The interface strength is determined by the additive composition and impurities [75].

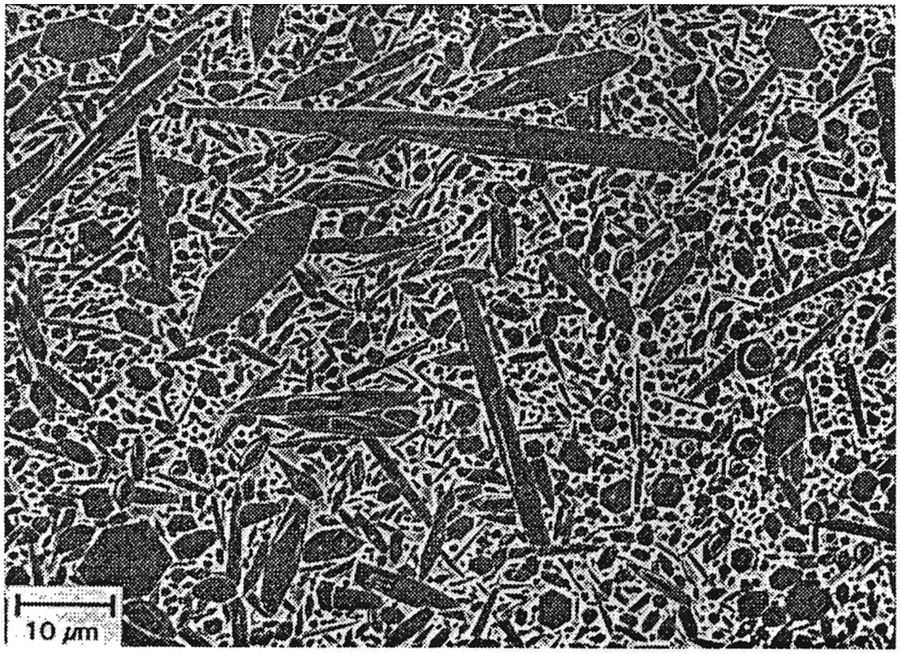

**Fig. 1** Scanning electron micrograph of a gas-pressure sintered silicon nitride ceramic after plasma etching. The micrograph shows elongated $Si_3N_4$ grains embedded in a matrix of fine, equiaxed grains and a grain-boundary phase (reproduced from ref. 80).

Another particularly difficult compromise exists between the requirement for sinterability and grain anisotropy, favored by the liquid-phase assisted sintering, and requirement of high-temperature strength and creep resistance that is limited by the viscous flow of the silicate liquid. Thus, one of the most significant microstructural features is the elimination of liquid residues either within a monophase solid solution (i.e., transient, liquid-phase sintering) or by complete crystallization of the liquid in a diphasic ceramic microstructure by post-sintering heat treatment. The second approach is preferred [76].

Much research has been devoted to the understanding of nucleation and growth of anisotropic $Si_3N_4$ grains with a high aspect ratio (length/width) of > 5/1 in ceramic microstructure. There are two modifications of $Si_3N_4$: trigonal $\alpha$-$Si_3N_4$ and hexagonal $\beta$-$Si_3N_4$. It was found that the development of elongated grains is related to the $\alpha \rightarrow \beta$ transformation [77]. It became common practice to use $\alpha$-powders when anisotropic structures for high fracture toughness materials are desired.

Both $\alpha$- and $\beta$- type $Si_3N_4$ crystal structures form stable solid solutions with $Al_2O_3$. The solid solutions are known under the acronym "sialons" [78,79]. The microstructures of high performance sialon ceramics consist of equiaxed $\alpha$-sialon grains with a high hardness, $\beta$-sialon grains with an elongated morphology to achieve *in situ* toughening, and a grain-boundary phase which can be devitrified [80]. The most popular sialon composite based on $Al_2O_3$-$Y_2O_3$ additive contains yttrium-aluminum garnet ($3Y_2O_3 \cdot 5Al_2O_3$) as the crystalline grain-boundary phase. The material has negligible amounts of residual glass, due to wide solid solubility in the mixed $\alpha$ and $\beta$-sialon matrix, and exhibits good room- and high-temperature properties [81].

In tailoring the properties of complex sialon ceramics, knowledge of high-temperature phase equilibria is indispensable. Figure 2 shows relatively simple phase relationships in "pure" $Si_3N_4$ ceramics. Preferred compositions are on the diphasic $Si_3N_4/M_2Si_2O_7$ tie-line or within the $Si_3N_4$–$Si_2N_2O/M_2Si_2O_7$ compatibility triangle (M = Y, Nd, La, most frequently Y). From the diagram it may be seen that with $Si_3N_4$ powders with low impurity oxygen content the proper composition can only be achieved with $SiO_2$ powder additions, in proportion to $Y_2O_3$ additive level. Outside the com-

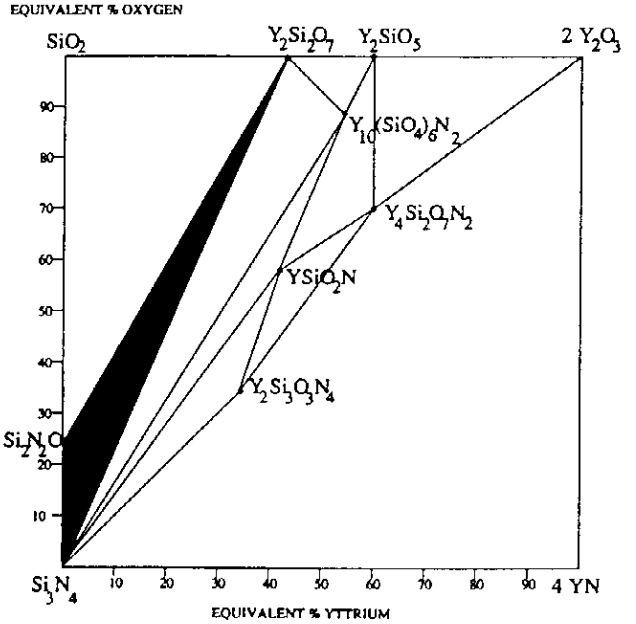

**Fig. 2** The preferred compatibility triangle in the Y–Si–O–N system, favoring the crystallization of $Y_2Si_2O_7$ polymorphs as grain-boundary phases (reproduced from ref. 82).

patibility triangle other oxide-nitride phases occur which tend to oxidize at high temperatures in air, resulting in ceramic degradation due to accompanying change in atomic volume.

The representation of phase equilibria in the quasi-quinary system M–Si–Al–O–N is much more complex. The results are presented in the form of a Jänecke prism [82,83], Fig. 3, showing the important solid solutions in the system: α-$Si_3N_4$, α- and β-sialon, and potential intergranular phases formed by glass crystallization. Typical compositions for sialons are in the ternary eutectic niche in $Y_2O_3$–$Al_2O_3$–$SiO_2$ system with nitrogen solubility and glass formation to 20–30 equivalent percent.

On the basis of accumulated knowledge, the following steps in designing $Si_3N_4$-based engineering ceramic materials have been formulated [84].

1. Phase diagram: The composition range leading to a liquid phase under $Si_3N_4$ sintering conditions should be chosen. The constitution of the grain-boundary phase of $Si_3N_4$ should be defined to give rise crystallization by a suitable heat treatment.
2. The microstructure of the material should be designed to include mainly $Si_3N_4$ crystals, a controlled range of grain size, a preliminary and crystallized composition of matter at the grain boundary, and the thickness of the grain-boundary phase.
3. Finally, the processing parameters should be optimized to satisfy the above requirements.

The example of $Si_3N_4$ ceramics clearly shows the deciding influence of chemical reactions in all steps of the manufacture of complex high-performance ceramics. It also demonstrates the fact that the specifics of each system have to be studied in detail to understand and properly design the manufacturing route.

### 4.5. Grain boundaries, interfaces, and segregation phenomena

Interfaces (free surfaces) and grain boundaries in ceramics often exhibit solute segregation. The effects are diverse and frequently influence the properties of ceramics both indirectly and directly—indirectly

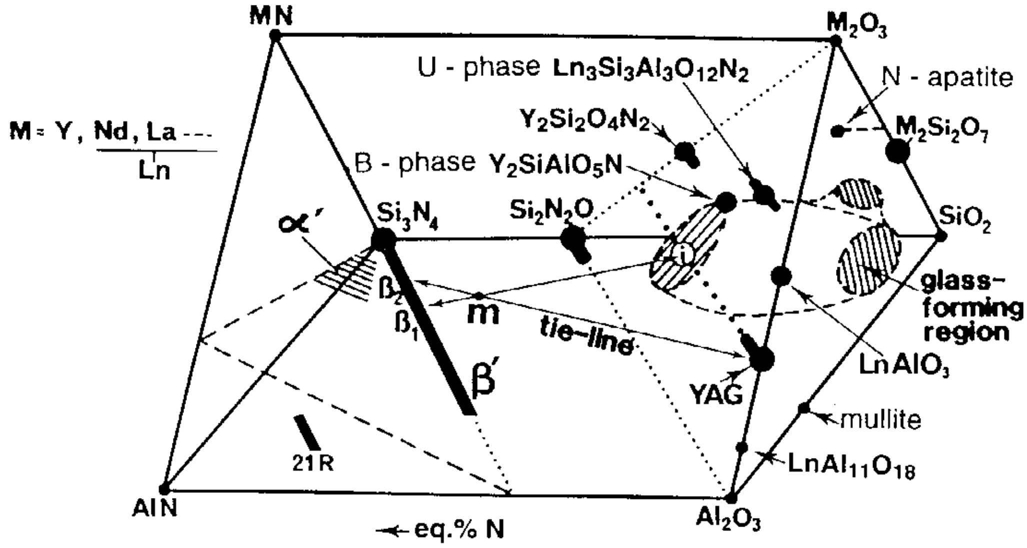

**Fig. 3** Jänecke prism representation of M–Si–Al–O–N systems showing the relation between major ceramic phases (α-$Si_3N_4$, α and β-sialon) and potential inter-granular phases formed by glass crystallization (reproduced from ref. 82).

by acting on microstructure development during sintering and directly by influencing the electron transport in ceramic products.

Generally, segregation of dopants or impurity atoms toward grain boundaries restrains or inhibits the grain growth. This is known as “impurity drag effect” [85]. Such fine-grained ceramics may exhibit superior mechanical properties, provided the segregation does not interfere with the diffusional mass transport necessary for densification. Unfortunately, the segregation toward various crystal planes may not be homogeneous, resulting in heterogeneous microstructures.

The type and amount of solute segregation at interfaces directly influence many electrical, dielectric, and magnetic properties of ceramics. For example, polycrystalline ceramics that are widely used in electronic devices, such as thermistors and varistors, rely on electrically active interfaces and grain boundaries for their unique operating characteristics, properties that do not exist in monocrystals [86,87]. The positive temperature coefficient (PTC) of resistance observed in donor-doped $BaTiO_3$ and nonlinearity of current-voltage dependence in ZnO-based resistors are a direct result of processes that are still poorly understood, but are associated with grain boundaries [7]. Metal–metal oxide interfaces that can exhibit ohmic or rectifying electrical properties play an essential role in metal-supported catalysts and in environment-sensitive devices and sensors.

The significance of surfaces and interfaces for the processing of ceramics with desired microstructures has long been recognized [88]. Considerable progress has been made in the understanding of interface structures in recent years, and this has been well covered in reviews [89,90]. The structure of grain boundaries is understood at a considerably less detailed level. The main obstacle to understanding these boundaries is their complexity due to impurities and dopants. Difficulties encountered in predicting the influence of these foreign atoms on the boundary mobilities are severe [87,88].

1. Segregation can arise from different causes. The distribution of species in the segregation regions can accordingly take different forms.
2. Segregation at interfaces can be highly anisotropic with different degrees of segregation arising at crystallographically different interfaces [91].
3. The direct link between the degree of segregation and boundary kinetics [92] is difficult to establish experimentally. Grain growth studies [52] indicate that the influence of segregated additives can be very considerable; direct measurements are, however, difficult and are complicated by the existence of instabilities (i.e., dependence of the mobility on the local driving force for migration).
4. Mobility can be influenced by other factors such as second phases or attached porosity [93].

At present, some common rationales seem to emerge, such as the influence of additive size on segregation [94] and the influence of additive charge in controlling boundary mobility [95]. A comparison of observations reported for different systems makes it possible to estimate the relative significance of the two factors [96].

The nature of grain boundaries with segregated layers is best studied in semiconducting and ionic conducting ceramics. Grain boundaries commonly act as paths of rapid transport for ionic species and as barriers to the conduction of electrons. The defect chemistry of the grain boundary region under equilibrium and nonequilibrium conditions is the controlling factor for transport both across and along grain boundaries. Grain boundaries in electroceramics are generally nonstoichiometric and the resulting electrostatic potential [97,98] represents an important driving force for the segregation of impurities and dopant ions. Therefore, the identity, concentration, and spatial distribution of grain-boundary atoms and defects is of greatest interest for the optimization of electrical properties of functional ceramics. It is hoped that the combined use of electron microscopy and electrical property measurements such as impedance spectroscopy may (i) allow for the identification of grain-boundary defects, (ii) clarify their role in determining the properties of electronic ceramics, and (iii) contribute to a general understanding of segregation phenomena on microstructure development during the sintering of ceramics.

Another important issue not well understood in processing semiconducting ceramics such as varistors and capacitors is the nonequilibrium defect distribution established during cooling from processing temperatures. Important information on the nature of segregated layers may be obtained by studying the dependence of electrical properties as a function of cooling conditions, such as cooling atmosphere and rate of cooling. In electroceramics, processed at high temperatures but intended to be used at lower temperatures, such as varistors and thermistors, the properties critically depend on nonequilibrium defect distributions at the boundaries established during cooling from the processing temperatures. At present, the formation of defects at boundaries and interfaces during the most common processing step, oxidative cooling in an air atmosphere, is poorly understood. The temperature dependence of the concentration of ionic species, their diffusivity and stoichiometry in segregated layers are expected to play the crucial role. However, conclusive experimental studies are limited.

Systematic studies of segregation phenomena, particularly on a quantitative basis, are still very much required in order to understand the influence of impurities and dopants for the control of coarsening and the properties of the final ceramics. It is hoped that comparisons of data from many different systems will eventually establish a basis for a more rational choice of dopants for manipulating and controlling specific properties.

## 5. NEED FOR RELIABLE DATABANKS RELATED TO HIGH-TEMPERATURE REACTIONS OF INORGANIC COMPOUNDS

Optimization of the high-temperature processing of specific chemical compositions into ceramic articles involves a proper choice of processing parameters, such as the type and amount of dopants, heating rate, time and temperature of sintering, and the nature of the processing environment. The environment may be a low- or high-pressure gas, and the gas could range from chemically reducing to oxidizing. It could include sample container materials or gaseous species that chemically react with the processed parts, or are chemically inert.

The processing parameters are determined in the development stage of the product. The parameters may be determined experimentally. However, the rational way requires knowledge of thermodynamic and kinetic data for chemical reactions which take place, or may take place, during the high-temperature processing steps of the ceramics. It is of paramount importance that in the development stage of the ceramic product, the possible minor deviations of the designated processing parameters are identified, and their influence on the properties and reliability of the finished product are recognized. The economy and reproducibility of production lines directly depend on such knowledge.

A knowledge of chemical reactions in ceramic systems at high temperatures is particularly demanding since small variations in temperature strongly influence the kinetics of reactions and may drastically change reaction mechanisms of importance to sintering.

In 1989, Brewer [99] analyzed the importance of chemistry in high-temperature materials and technology and stressed the need for reliable databanks on high-temperature reactions. The availability of data, such as enthalpies of formation, entropies and high-temperature heat capacities, make it possible to predict the high-temperature behavior. Of particular importance are deviations from predicted behavior, which may be taken into account by phase equilibria determinations.

Of particular value are studies of systematic trends for a sequence of elements in the periodic table, thus enabling more reliable predictions of chemical reactions and properties for ceramic systems involved in manufacture when no data are available [13,14].

For ceramic engineers and scientists it is often a demanding problem to retrieve, critically evaluate, and combine the significant information from the exponentially growing literature. Finding and analyzing papers dispersed in many journals and published in many languages is a tedious and time-consuming job. An even more serious obstacle is the need for broad professional experience to be able to critically evaluate the reliability of reported data and the correctness of the stated conclusions. Unfortunately, a considerable fraction of the data in primary literature is unreliable and in contradiction.

Most professionals involved in ceramic manufacture and development are not familiar enough with experimental techniques of high-temperature measurements and theories to be able to critically evaluate the various, often conflicting, results.

Thus, it would be of great significance to the ceramic community if each user of data would not need to take the time to search the literature independently, but could take the data from an assessed databank. Even more important for the user would be to know a source of very reliable data so as not to be misled by erroneous values. A wrong choice between divergent values could make the difference between the success or failure of an intended process. Therefore, reliable databanks of chemical and thermodynamic and kinetic properties that have been prepared by persons with adequate background to critically evaluate the data would save great amounts of time and money in developing optimized ceramic processing parameters.

## 6. IMPORTANCE OF PHASE EQUILIBRIUM STUDIES

The importance of the availability of reliable phase diagrams to the development of advanced ceramics cannot be overstated. These graphical representations of the chemistry and thermodynamics of a system summarize a wealth of information of critical importance to efficient ceramic processing. Phase equilibria information has been a prime factor in the improvements evidenced in ceramic technology. Modern traditional ceramics, refractories, glass, cements, whiteware and the like, exhibit greatly improved properties over their predecessors, due in large measure to the availability of appropriate phase diagrams. The newer classes of advanced ceramics are dependent even more on phase diagrams to guide their processing since end-use property requirements are tightly constrained within narrow limits.

Ceramists are well aware of the importance of phase equilibrium data, and a worldwide phase diagram development program was initiated by the American Ceramic Society, in collaboration with U.S. National Institute of Standards and Technology (NIST) to provide an evaluated, up-to-date, computer-stored database of phase diagrams to the ceramic community [100]. There are two problems concerning this phase diagram database. First, data on multicomponent systems are lacking, and second, the accuracy and precision of the published diagrams is frequently questionable. Also, most of the phase diagrams of systems have not been critically compared to their respective thermodynamic properties.

Phase diagrams suffer from many potential sources of error. A diagram as a whole represents the sum of a great deal of thermodynamic information and must, therefore, be consistent not only with these data but also must be internally self-consistent. In particular, it must always obey the phase rule. The vast majority of phase diagrams appearing in the literature are experimentally determined. However, it must be noted that, in general, insufficient thermodynamic data exist to permit an independent check on the accuracy of experimentally determined diagrams. Table 5 taken from ref. [101] lists some of the major types of inaccuracies that occur in published phase diagrams.

The recent development of experimental techniques for investigation of the phase diagrams of ceramic materials has greatly improved the reliability of data. Many problems that handicapped such studies in the past have either disappeared or have been mitigated. The problem of achieving reliable temperature control has all but vanished with the advent of cheap, dependable electronic instruments. The generation of high temperatures has expanded from classical methods of resistance heating to laser heating, use of imaging furnaces, fast pulse heating generators, and others [102]. The purity and reliability of chemicals has greatly improved. Very small samples, and individual grains, can be investigated using electron microprobe analysis, transmission electron microscopy, or other related techniques. The sensitivity and quality of X-ray diffraction has been improved by the advent of modern diffractometers and focusing cameras [101].

What systems need to be studied to advance ceramic technology? The value of previous studies made on oxide systems is well recognized, but much work remains to be done. The effects of minor constituents will continue to be evaluated, and systems relevant to the application of newly developed

**Table 5** Inaccuracies in phase diagrams [101].

| Features | Error source |
|---|---|
| Internal consistency | Phase rule is not obeyed |
| External consistency | Inconsistent with related literature |
| Choice of system | Volatilization, decomposition, oxidation state changes, etc., have influenced results. |
| Choice of experimental conditions | Equilibrium not attained.<br>Reaction between container and sample occurs.<br>Lack of chemical analyses.<br>Inadequate characterization techniques. |
| Specific features: | Subsolidus equilibria not checked.<br>Compound has incorrect formulae.<br>Solid solution limits or variations in stoichiometry incorrect.<br>Polymorphic changes in solids and immiscibility in melts not determined. |

materials such as high-temperature superconducting, microwave materials, and ceramic sensors need to be determined. Among the specific features of oxide phase diagrams which must receive more attention are the accurate determination of solid solution limits, the compositions of coexisting solid solutions, examination of the subsolidus phase relationships, and the presence or absence of liquid immiscibility at high temperatures. Systems of metals with oxygen are also a comparatively neglected area that require phase equilibria studies under reducing conditions.

However, the world of ceramics includes many non-oxides. Carbides, nitrides, silicides, borides, and sulfides are among the newer ceramic materials that are well recognized, and deserve more systematic study. These studies should include the two objectives of first, examine the chemistry of most relevance to materials synthesis, and second, determine the chemical interactions most likely to arise when the ceramics are subjected to service conditions.

## 7. CONCLUSIONS

Most of the advanced ceramics are polycrystalline, and the properties depend on the microstructure that develops during the sintering operation. Optimization of processing of contemporary ceramic materials demands the knowledge of interrelationships between fabrication parameters, microstructural development, and properties.

The physical basis of sintering and microstructural development is well established. The theory of sintering and grain growth is scientifically sound and experimentally tested. The parameters needed to be taken into account in optimizing the processing of ceramics are defined and their role explained in theoretical models for sintering and grain growth. They include surface energies, diffusion coefficients, interfacial reaction coefficients, and vapor pressures, all as a function of temperature and chemical composition.

Important aspects not included in general sintering models are the chemical reactions that occur at processing temperatures. Starting ceramic compositions are frequently designed to be chemically heterogeneous, and even commercially pure, monophase ceramics contain impurities. Chemical heterogeneity of unfired ceramic products gives rise to chemical reactions at firing temperatures that compete with the physical forces for densification and microstructure evolution.

To predict and control the influence of dopants and impurities, the mechanisms and parameters of high-temperature reactions and their influence on surface energy, grain-boundary energy, interphase energy, surface diffusion coefficients, boundary and lattice energy coefficients for a range of specific ceramic systems are needed. Since data on specific systems are rare, generalizations and systematic trends based on chemical systematics are of particular value.

A knowledge of chemical reactions that take place during sintering, and the availability of data on high-temperature phase relationships are the basis for understanding important phenomena in ceramic processing such as the densification kinetics, and the development of microstructures of semiconducting grain boundary-controlled functional ceramics and tough ceramics. It is important to understand the origin of secondary phases, the effect of impurities on mechanical and electrical properties, and property changes of ceramics induced by service conditions. Knowledge and control of chemical processes that occur during ceramic processing are necessary to surmount the main obstacles for wider use of technical ceramics. The primary obstacles include insufficient reliability, reproducibility, and high cost. Knowledge of the listed interrelationships, and others mentioned previously in this article, is necessary to open the numerous new applications. Developing such knowledge presents a great challenge to chemists at the turn of the century.

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