

Ceramics by the Solution-Sol-Gel Route

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The use of solution mixing followed by gelation to make ultrahomogeneous glasses and ceramics of various oxide compositions for laboratory experimentation, with first organic and later principally colloidal inorganic, precursors was developed over 30 years ago. Major technologies that use the solution-sol-gel route have been developed to make nuclear fuel pellets, ceramic fibers, thin coatings, and abrasive grain. This article reviews the early history and summarizes present research in this field, particularly new processes aimed at achieving xerogel precursors of maximum heterogeneity with respect either to composition or to structure. Such nanocomposites provide major advantages in lowering sintering temperatures, refining microstructure, and controlling morphology and final phase composition.

MATERIALS RESEARCH HAS ADVANCED PRINCIPALLY BY the creation of new materials. It forms a classic example of Price's thesis (1) that technology, often by means of new instruments, advances science. In this case, new materials fulfill the role of new instruments. Ceramics made by the solution-sol-gel (SSG) route are a subset of new materials made by atomic-scale mixing of the constituents.

History of Solution-Sol-Gel Science and Technology

Ceramics—polycrystalline inorganic solid bodies consisting of one or more phases—have been made since time immemorial by mixing fine-grained solid powders, usually oxides such as SiO_2 , Al_2O_3 , Fe_2O_3 , or compounds thereof, and then allowing them to react in the solid state at temperatures between 1000° and 1500°C for periods of hours to days. The innovation of making ceramics and their noncrystalline analogs, the common glasses, by mixing the components in solution was basically a post-World War II innovation. The SSG process has three key parts: (i) mixing various oxides in solution, often with the use of metal organic precursors; (ii) forming a sol and causing it to gel as the key step in the process to retain chemical homogeneity during desiccation; and (iii) shaping during or after gelation into essentially final shape before firing. The development of the SSG process for scientific studies in ceramics took place between 1948 and 1956 (2). The key steps in the development of the technological process took place in the mid-1960s when several corporations took this “on the shelf” science and learned how to shape the gel to essentially final shape and to

make a variety of useful products. Another decade passed before these technological innovations stimulated new scientific research in the field, making SSG research one of the major foci of ceramics research in the 1980s.

Classical colloid science of ceramics. In the late 19th century chemists focused their attention on colloidal sols, microscopically homogeneous “permanent” suspensions of solid particles in a liquid. The early European work by T. Graham, H. Freundlich, T. Svedberg, and others is summarized by Zsigmondy (3). Yet the bridges between colloid chemistry and ceramics remained essentially nonexistent outside the field of forming clay bodies. Similarly, in the United States, although colloid chemists such as H. B. Weiser and W. O. Milligan (4) also worked extensively on oxide sols and gels, there was at best only a vague connection between these chemical studies and ceramic science or technology.

The next step in applying colloid science to ceramics was taken in efforts toward synthesizing clays. Ewell and Insley (5) conducted studies of coprecipitated gels of Al_2O_3 and SiO_2 , electrolyzed to remove Na^+ , as starting materials for kaolin synthesis. A benchmark in the summary of research on sols and gels of silica and the silicates was Iler's Baker lectures at Cornell University. Iler's book (6) discusses the chemistry of synthesizing micas and clays by the SSG route (7). The first application of sol-gel (SG) methods for the production of chemically homogeneous anhydrous ceramics—bulk glasses in this case—appeared in a paper by de Korosy (8), who used sodium aluminate–sodium silicate coprecipitation as the basis for making a gel precursor for melting to a glass.

Making homogeneous ceramics and glasses. Through the early post-World War II era, making ceramics or glasses for laboratory research required tedious mixing of powders and long periods of heating or melting, typically several times in succession with regrinding between meltings. In 1948, a new approach was taken in my laboratory to making pure, anhydrous, homogeneous, glassy, and crystalline one- and multicomponent 5- to 10-g samples of ceramics or glasses. The component ions were mixed in solution, thereby achieving mixing on a 0.5-nm scale instead of as 50- μm solid particles—a gain in intimacy by 10^4 or 10^5 . The coprecipitation route, which was also being exploited to make beads of aluminosilicate gels for cracking catalysts, trapped too much alkali to make pure solids. Moreover, it was impossible to find inorganic salts, especially of tetravalent and pentavalent ions, that did not separately react or precipitate in a multicomponent system. Therefore, starting with the system Al_2O_3 – SiO_2 , Roy and Osborn (9) used metal organics as the sources of many of the common ions. Tetraethyl orthosilicate, aluminum isopropoxide, and tetrabutyl titanate were used as key sources of silicon, aluminum, and titanium. The method for making ceramic powders and glassy melts was successively generalized from the two-component to a three-component (MgO – Al_2O_3 – SiO_2) system (10) and to titanate systems including TiO_2 – SiO_2 , BaO – TiO_2 – SiO_2 , and BaO – CaO – TiO_2 – SiO_2 (11). In the large number of mineral syntheses and phase equilibrium studies carried out at Pennsylvania State University in the 1950s and 1960s, virtually any

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Table 1. Nanocomposite combinations; NCS, noncrystalline solid.

NCS host + NCS dispersoid	NCS host + crystalline dispersoid	Crystalline host + crystalline dispersoid
SiO ₂ + (AlOOH) _n + AlPO ₄ + (NdOOH) _n	SiO ₂ + AgCl + CdS + BaSO ₄ + PbCrO ₄ + Cu + Ni	Al ₂ O ₃ + Ni + Pt + Cu ZrO ₂ + Cu + Pt

composition, even five-, six-, or seven-component systems, was prepared by the SSG route. The fine noncrystalline xerogel powders (anhydrous solid phase with collapsed microstructure) were typically and routinely (i) melted to glass where possible, (ii) hydrothermally crystallized to fine ceramic powders with a degree of structural order unattainable by any other process (2), and (iii) crystallized dry to a ceramic aggregate (although not as a shaped, desired product). Later in the development of the SSG method, to avoid possible loss of some ethyl orthosilicate vapor during the 75° to 90°C hydrolysis and gelation, an alternate source of SiO₂, an inorganic SiO₂-sol (Ludox, 35% of which consisted of 20-nm particles of "SiO₂" dispersed in H₂O and stabilized by NH₄⁺) was used. These and similar commercial sols of "Al₂O₃" and ZrO₂ came into regular use as the simplest route to gel manufacture and produced products at high temperatures that were virtually indistinguishable from those made from organometallics.

The SSG method for making oxide glasses and ceramics in the laboratory was widely adopted in experimental geoscience (12). By 1960, the following data had been experimentally established.

1) The SSG process, with either organic precursors or very fine (20 to 200 nm) sols of SiO₂, "Al₂O₃," or ZrO₂, could be used to make ultrahomogeneous, slightly hydrated or anhydrous oxide ceramics of any composition.

2) Such powders, when heated dry in the range of 500° to 1000°C, typically yielded anhydrous noncrystalline oxide xerogel materials (which rigorously cannot be called glasses), extending the compositional range of noncrystallinity far beyond that attainable by the routine or the more recent rapid solidification liquid-to-solid (glassmaking) or vapor-to-solid (sputtering) routes.

3) Many such powders could be hot-pressed at modest temperatures to make noncrystalline ceramics of compositions ranging from SiO₂ to those of extraordinarily refractory compositions including ThO₂ and ZrO₂.

4) Some of these xerogels could be "melted" to ultrahomogeneous glasses at temperatures hundreds of degrees below the normal melting range.

During this period the interest of colloid chemists began to converge with that of ceramists in the preparation of concentrated

sols of many oxides and in their gelation. In brief, pH, salt concentrations, and water/solid ratios can be manipulated to give a wide variety of microstructures in gels (6, 7). Matijevic (13) learned how to control a wider range of compositions (including transition metal oxides and sulfides) and size (especially monodisperse sols) and morphology.

The SSG Process for Making Ceramics

Figure 1 shows the essentials of the generic SSG process and how it is used to make a variety of ceramic materials.

Step 1. Components are put into solution. The "solution," which in a multicomponent composition is a true ionic or molecular solution, makes possible the atomic-scale mixing that is the basis for the "ultrahomogenization" of the SSG technique. The liquid phase for the vast majority of oxide gels is water or a short-chain alcohol, and the solutes may be either inorganic nitrates, inorganic chlorides, or a wide variety of metal organic molecules.

Step 2. Conversion to a sol is accomplished by adjusting the activity of some species, H⁺ and OH⁻ and other ions, which results in the formation of a dispersed solid phase. In many cases a stable sol (already formed in step 1) is one of the starting materials for the next steps, so that there is no true solution in step 1 at all. In some cases we have shown by magic angle spinning nuclear magnetic resonance (MAS-NMR) that reaction between solution and dispersed solids can occur; Al³⁺ ions, for example, from the solution can enter the tetrahedrally linked solid SiO₂ particles (14).

Step 3. Gelation of the sol is controlled principally by pH, ionic strength, temperature, and time. Manipulation of these parameters is an empirical procedure that must be worked out for each composition. Although the general conditions of pH and temperatures are known for simple oxides such as SiO₂ and AlOOH, the fine tuning of this step for different starting materials, especially new organic precursors, and multicomponent systems has become a major area of current research.

Step 4. The key step in the technological utilization of the SSG process is the shaping of the viscous sol or gel. Since the 1970s, each family of SSG technological inventions has had a different process for shaping the viscous sol or gel (while still in the viscoelastic or plastic regime) to the respective final desired shape or form. Final gel shapes include spheres, fibers, thin sheets (coatings on a substrate), and small "cubes." Each of these shapes has led to the development of a substantial new technology.

Step 5. Desiccation and heat treatment lead to a xerogel and finally to a glass or ceramic. The processing here varies depending on the product being made, but in all cases the highly reactive nature of the xerogel assures that the time and temperature of reaction are both dramatically lowered by comparison with the conditions of traditional ceramic processes.

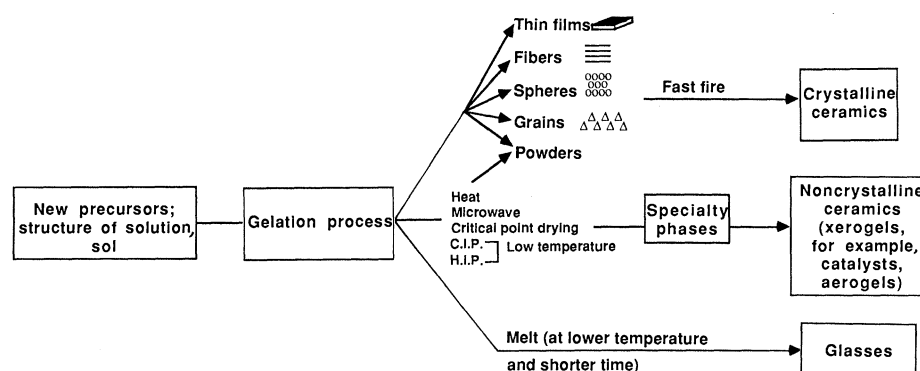


Fig. 1. The solution-sol-gel process for making ceramics (broken down into discrete research steps or areas); C.I.P., cold isostatically pressed; H.I.P., hot isostatically pressed.

Table 2. Densities of single-phase and diphasic gels.

Starting materials	Density at 1200°C (g/cm ³)	Density relative to mullite (%)
Single-phase: Al(NO ₃) ₃ · 9H ₂ O + Si(OC ₂ H ₅) ₄	2.71	85.4
Diphasic: AlOOH + Si(OC ₂ H ₅) ₄	2.92	92.0
Diphasic: AlOOH + Ludox (SiO ₂)	3.05	96.2

Up to the present, the maximum dimensions of any commercial, densified ceramic product made by the SSG process have been limited to a few millimeters in three dimensions (spheres or cubes), a few micrometers in two dimensions and large in the third dimension (in the case of fibers), and 10 μm or less in one dimension and large in the other two dimensions (in the case of coatings). The limitation in the size of ceramic objects made by the SSG route is due to the necessity for extracting the liquid phase and maintaining coherence and integrity during that step.

Existing Technologies Based on the SSG Route

The major classes of existing SSG technologies are described below.

Fuel pellets. In 1960, Mumpton and Roy (15) used the SSG process to make highly reactive ceramic powders for the study of reactions and phase equilibria in the system UO₂-ZrO₂-ThO₂. In the mid-1960s, a group at Oak Ridge National Laboratory conceived and executed the first purposive shaping of the gel of these same compositions into small spheres (16) for use as nuclear fuel, by causing gelation to occur while a spherical drop of the solution of uranium or thorium was falling slowly in a long column of a heated second organic liquid with which it was immiscible but which caused its hydrolysis to the solid oxide.

Fibers. The industrial capacity to make fibers 5 to 10 μm in diameter containing principally polycrystalline Al₂O₃, mullite (3Al₂O₃·2SiO₂), and various polyphasic assemblages, starting with inorganic solutions and sols, was well established and patented in the 1970s in the work of Imperial Chemical Industries, Du Pont, 3M, and Carborundum researchers. The appropriate gel is extruded through orifices or is spun, and the fibers are dried and fired to form fibers that are strong at high temperatures, for example, with tensile strengths of 1.3 to 2.0 GPa for Du Pont FP Alumina fibers (17). A

recent summary by Birchall *et al.* (18) shows detailed microstructural and x-ray structures of alumina fiber at various stages of processing. As in virtually all SG-derived ceramics reacted at relatively low temperatures (1000° to 1200°C) for a few minutes, there is a mixture of submicrometer-sized crystals with a noncrystalline (not strictly a "glass") second phase.

Nonoxide fibers. The pioneering work by Yajima *et al.* (19, 20) on SiC fibers was not an example of a true SSG process, since polycarbosilane polymer is a viscous melt or solution, not a sol. In 1976, Yajima demonstrated the production of a high-temperature ceramic ("SiC") continuous fiber by polymerizing dodecamethylcyclohexasilane, which was spun into an organosilicon fiber and pyrolyzed at temperatures above 1000°C. The so-called "SiC" fiber (Nicalon) is a multiphasic fiber consisting of very fine, poorly formed SiC crystals in a noncrystalline matrix of Si-C-O-H-N with the SiC content often no more than 90 to 95 atomic percent. Yajima *et al.* (19) have influenced modern SSG research by demonstrating the possibility of pyrolyzing metal organic polymers (20) (or gels) to a ceramic. The ceramic is made by pyrolysis and destruction of all the original structure of the "organic" precursor. Tensile strengths of 3.3 GPa and a Young's modulus of 300 GPa have been routinely achieved, and the resistance to oxidation (compared to that of carbon fibers) has made SiC fibers a prototypical "high-tech" ceramic.

Coatings. The Schott Company in West Germany has been working on the SG coating of glass since before World War II, and their patents (21) and a series of papers by Dislich and colleagues (22) provide some details on the production of thin (≈1 μm) coatings of SiO₂ and TiO₂ on glass for reflective and antireflective effects. In recent years ~10⁵ m² of window glass have been coated annually by this company by the SSG process (most of the gold-colored windows in cities are coated by this process). Yoldas (23) made high-performance coatings of "TiO₂" by controlling the polymerization of the inorganic gel, but the thickness of the coating was also limited to ~1 μm. Although useful thin ceramic coatings are common commercial articles, efforts to make useful thicker (>10 to 25 μm) SG-derived nonporous coatings with both organic and inorganic starting materials have failed.

Bulk ceramic glass and abrasive grain. Dense bulk ceramics have not been made successfully from a gel. Making bulk glasses is a straightforward matter of melting large amounts of xerogels. In the early 1970s the Owens-Illinois Company explored experimentally the costs and benefits (mainly ultrahomogeneity and lower melting temperatures) of making full-scale tank melts through the SSG process (24). Just before the cost of oil increased, the process was

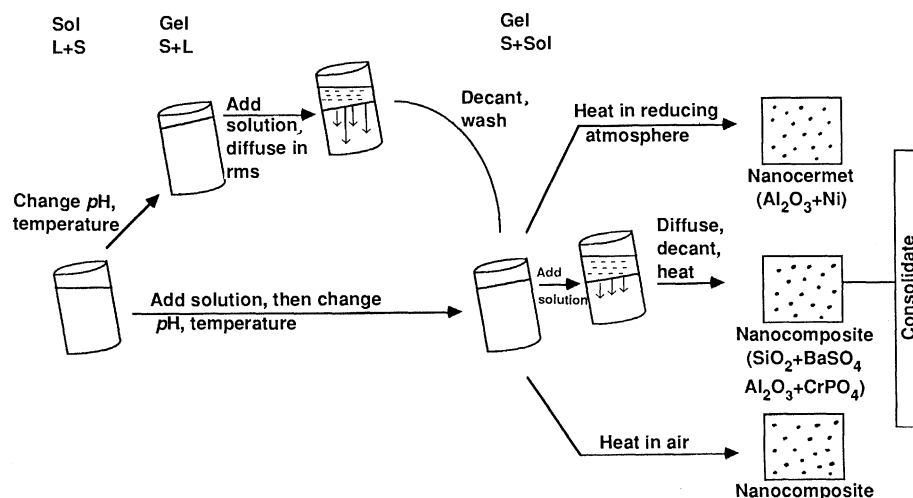


Fig. 2. Schematic of the gel impregnation method for making a diphasic xerogel or nanocomposite; S, solid; L, liquid.

judged to be uneconomical and work was terminated. More recently, Pope and Knox (25) exploited the lower melting temperatures (1300°C) made possible by SSG to melt large monoliths of an aluminosilicate radioactive waste glass that was more chemically resistant than the reference borosilicate glass. Traditional melting methods could not have retained many of the volatile elements in radioactive waste at the temperatures required to melt and homogenize the aluminosilicate glass made from traditional starting materials.

The maximum-dimension ceramic technological product that is SSG-derived is the new "Al₂O₃" abrasive grain for grinding wheels developed by Leitheiser and Sowman (26). The SG process in this case avoids both the extremely high temperatures (>>2000°C) required to melt the "Al₂O₃" and the enormously expensive step of crushing and grinding centimeter-size pieces of extremely hard material into the millimeter-size range.

Current SSG Research

In the last decade, research on SSG science has accelerated worldwide, and an excellent cross section of contemporary research can be found in the proceedings of biennial conferences on this topic (27). One can comment on the trends in recent work connecting it to the various steps of the SSG process shown in Fig. 1. This work has not resulted in many new materials.

Polymer chemists have been active in synthesizing new polymers as precursors for ceramics (28), but only a small proportion of tailored polymers has yielded any recognizably new materials. One such application is the precise control of stoichiometry (step 1) by having the two metal atoms in the same organic molecule. This has been achieved by Clabaugh *et al.* for BaTiO₃ (29) and Hirano for LiNbO₃ (30). (Deviations from stoichiometry are connected to degradation of LiNbO₃ in most electro-optic applications.) Other studies have concentrated on the synthesis of electronic ceramics. Special solutions (not usually sols) are designed from which the

desired phase—typically a perovskite or similar structure—will crystallize at the lowest possible temperature. Hirano (30) has made LiNbO₃ phases and Payne has made PbTiO₃ (31). Such low temperatures of formation of capacitor and active elements could be of great value in integrating ceramics into semiconductor device processing and could justify the cost of special precursor organics.

The "molecular structure" of the solution (step 2) and the understanding and control of the gelation process have been emphasized in recent research. The ratio of hydrolyzing solution to organic polymer is a universally recognized critical parameter (32).

Another current area of research has been directed toward making larger monoliths. Such success has been achieved in making closed-porosity glass that is high in SiO₂. These studies extend earlier work aimed at extracting water from the gel by controlling its microstructure; this was achieved by the use of "drying control agents" or critical point drying to avoid the formation of a meniscus. Transparent noncrystalline solids that are several centimeters in diameter and are stable to about 800°C have been made by Prassas and Hench (33). In a variant of this method, use was made of CO₂ near room temperature as the drying fluid by Tewari *et al.* (34) who used it to make optically transparent aerogel windows of modest size (several cubic centimeters) containing between 10 and 60% solid SiO₂ glass.

Some studies have been concerned with optimizing the process for making ultrahomogeneous and ultrapure glass with the minimum content of transition metal ions (35). Other papers discuss phase separation in the xerogels of compositions where the glass may or may not be known to phase separate (36).

Maximally Heterogeneous Materials or "Nanocomposites"

The principal goal of most investigators in the field and the most obvious advantage of SSG processing have been to make maximally homogeneous glasses and ceramics and also to use much lower temperatures and reduce the reaction times in the process. In 1982, however, our laboratory's goal was radically changed to using the SSG process to make maximally heterogeneous materials. "Maximally heterogeneous" here can be quantified by the surface area of the contact between the two (or more) phases involved. To attain such heterogeneity, a perfect dispersion and mixing of two (or more) solid phases and the subdivision of the latter on an extremely fine scale are needed. The term "nanocomposites" describes the materials derived by these SSG processes [the size of the individual phases is in the nanometer range (typically 10^{1±1} nm)].

There are two different approaches to making such diphasic xerogel nanocomposites. The first method (Fig. 2) is based on experience with crystal growth in gels (37). The goal then was to minimize nucleation and hence cause one or a few crystals to grow very large, while not exceeding the solubility product of the growing phase throughout most of the gel host.

In the nanocomposite studies the ratio of nucleation to growth was reversed, which made the ratio nearly infinite and caused uniform growth of "crystals" of the second phase 1 to 10 nm in size throughout the gel. With the appropriate solutions, Roy *et al.* (38) made nanocomposites of the combination of materials in Table 1. The composites of AgCl-SiO₂ are "0-3" composites [following the terminology of Newnham *et al.* (39)] that can be made into photochromic solids or coatings when dried at 50° to 100°C; they can also be used as precursor materials for melting into photochromic glasses of any suitable composition. The metal-containing composites were made by reducing the second phase (which was typically a hydroxide of a transition metal) in forming gas at 300° to

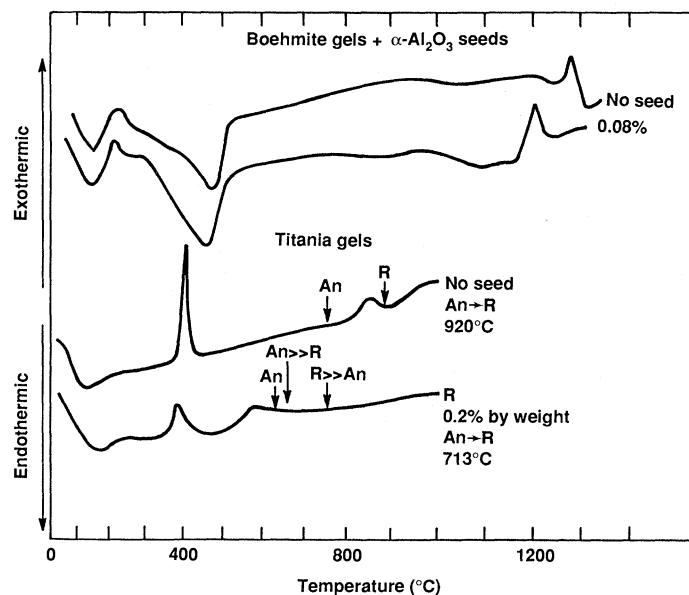


Fig. 3. DTA patterns (two upper traces) of noncrystalline single-phase, and structurally diphasic, alumina gels showing the striking lowering of the $\theta \rightarrow \alpha$ transformation temperature by the addition of ~1% of 0.1- μm $\alpha\text{-Al}_2\text{O}_3$ crystals. The analogous effect of TiO₂-[rutile] seeds on lowering the temperature of the anatase-rutile (An-R) transition in TiO₂-[NCS] gels is also shown (two lower traces) (arrows indicate the phases found by x-ray diffraction). These are the first recorded instances of solid-state epitaxy.

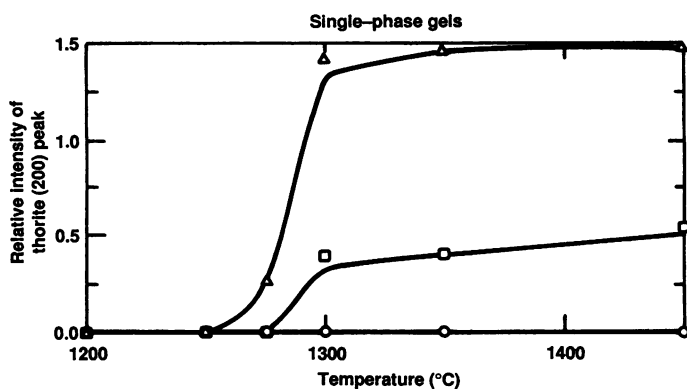


Fig. 4. Percentage of thorite phase formed, by x-ray diffraction, as a function of firing temperature in ThSiO_4 -[NCS] gels, seeded (made diphasic) by adding 1% of a sol of ThSiO_4 -[thorite] crystals (Δ) and by adding 1% of ThSiO_4 -[huttonite] crystals ($\circ$); unseeded sample ($\square$). At 1450°C one can obtain 100% thorite or 100% huttonite depending merely on the epitaxy.

500°C. Diphasic $\text{Ni-Al}_2\text{O}_3$ xerogels formed by this process can be sintered into nanocomposites with hardnesses of 20 GPa and fracture toughnesses near 5 to 10 MPa/m (40).

The second method for making nanocomposites is widely applicable to all ceramics. It requires the vigorous mixing of two sols (to assure that no rapid flocculation of one by the other occurs), gelling the mixed sol, and processing. Some remarkably useful nanocomposites have been produced; the SG technique is essential to the success of the method, since no other means can assure the homogeneous mixing of phases on such a small scale.

Epitaxy in Structurally Diphasic Ceramics

From a phase-rule viewpoint, two sols, one with a solid phase consisting of crystalline quartz and one with the usual noncrystalline solid (NCS) SiO_2 (such as in Ludox), when mixed and gelled and desiccated, make a structurally diphasic xerogel. Such "ultraheterogeneous" materials behave in an extraordinary manner with respect to their reaction temperatures and the microstructures of the product. The concept of using an epitaxial substrate, or seed, to accelerate the kinetics of formation of the thermodynamically stable solid phase, from solution, was introduced in our earliest SG work (41). Thus boehmite-structure gels were seeded with $\alpha\text{-Al}_2\text{O}_3$ and diaspore, and $\text{LiAlSi}_2\text{O}_6$ was seeded with α -spodumene, with acceleration of the formation of each of those phases in hydrothermal runs. This concept has been extended to solid-state processes. Figure 3 shows the differential thermal analysis (DTA) patterns of several xerogels comparing a single phase Al_2O_3 -[NCS] gel with a diphasic 99% Al_2O_3 -[NCS] + 1% Al_2O_3 -[corundum] gel (42). (The relevant terminology gives the chemical composition first followed by the structure in square brackets.) Even during the short time of the rapid heating (20°C per minute) of a DTA apparatus, the transition temperature and crystallization temperature of α -alumina was lowered by 100° to 150°C. By using a series of second phases of different crystal structures, we conclusively established (43) that this lowering of the crystallization temperature is a true structurally triggered (epitaxial) seeding effect, that is, catalysis in the solid state of the growth of a phase by provision of large numbers of nuclei with the structure of the desired phase (in this case).

Adding TiO_2 or SiO_2 sols as second phases to AlOOH gels has no effect. On the other hand, TiO_2 -[rutile] sol added as seeds to TiO_2 -[NCS] sols lowers the temperature of rutile crystallization by over 200°C. The clearest confirmation of the crystal structural control has been demonstrated (44) with ThSiO_4 -[NCS] gels, one mixed with

ThSiO_4 -[huttonite] and the other with ThSiO_4 -[thorite]. As shown in Fig. 4, at 1400°C the former yields 100% crystalline huttonite and the latter 100% crystalline thorite. Thus one can control even the phase of a ceramic body by simple SG processing. The epitaxial seeding works even in complex compositions and structures such as $\text{NaZr}_2\text{P}_3\text{O}_{12}$ (46), with a marked influence on both sintering and microstructure.

Diphasic SG effects on microstructure development are equally remarkable (45). Figure 5A shows the microstructures developed in a typical alumina gel fragment (of the abrasive grain size) in pure Al_2O_3 ; Fig. 5B shows the analogous experiment with the same parent sol phase mixed with 1% of the Al_2O_3 -[corundum] sol. The grain size drops from 10 to 20 μm to less than 1 μm .

Compositionally and "Doubly" Diphasic Gels—Reactive Sintering in Nanocomposites

By using mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) as the example, the sintering behavior of a single-phase xerogel [one derived from a homogeneous solution of $\text{Al}(\text{NO}_3)_3$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$] has been compared (47) with that of a second xerogel made from two separate sols that has been shown by MAS-NMR (14) to consist of separate alumina and silica phases. Table 2 shows the improvement in density obtained by using a compositionally diphasic gel in which the heat of reaction drives the sintering. When the compositionally diphasic mullite sol has added to it a third sol, which contains a third, structurally different solid phase (that is, crystalline mullite) and is then gelled, dried, and sintered, a remarkable change in morphology of the final crystals results. The equant grains of mullite in the

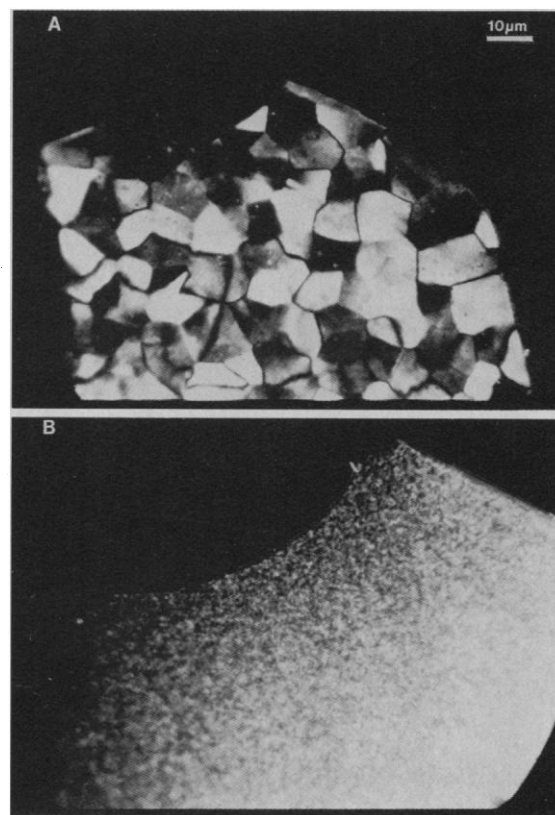


Fig. 5. Photomicrograph (crossed Nicol prisms) of microstructures of $\alpha\text{-Al}_2\text{O}_3$ formed from boehmite gels heated to 1200°C; (A) single-phase gel; (B) structurally diphasic gel "seeded" with $\alpha\text{-Al}_2\text{O}_3$. Note the dramatic grain size refinement from >15 to <1 μm .

sample with only two phases are replaced by mullite needles with an aspect ratio of 10:1, whereas the density attained is not affected. Thus, judicious manipulation of structural and compositional diphasicity (including crystallographic seeding) at the nanometer-size level appears to provide a novel process control mechanism for enhancing density, refining microstructure, and controlling the morphology of ceramic phases in bodies.

Natural Nanocomposites: Low-Temperature Chemically Bonded Ceramics

Nature abounds in micro- and nanocomposite structures that have toughness as a result of ceramic-polymer combinations. Examples include human bones and teeth where the 100-nm hydroxyapatite fibrils are topotactically related to the collagen phase. One other example is the 3:3 composite (39) of single-crystal CaCO_3 , and another polymer is the hard spines found in sea urchins and corals, from which "synthetic bones" that are compositionally and structurally similar to human bones have been prepared (48). The first tough hard ceramics made by a commercial SSG process were the synthetic opals produced in the 1960s by P. Gilson (49). These synthetic opals were made at temperatures below 100°C and were stable (50) to temperatures above 400°C. The microstructure and mechanical properties of Gilsonite synthetic opal have been examined (50). In the scanning electron microscope these opals are indistinguishable from natural opals; the microstructure of the wholly inorganic opal consists of clusters within clusters of small SiO_2 balls. However, Gilsonite is a true nanocomposite that consists of ~5% crystalline ZrO_2 and ~95% NCS- SiO_2 . Moreover, the transmission electron microscope revealed an extraordinarily regular arrangement of the much smaller (20 nm) ZrO_2 spheres within the "lattice" spaces formed by the face-centered cubic arrangement of larger balls. Gilsonite's optical properties appear to be directly derived from its diphasic nature, which may also contribute to its strength and toughness.

Conclusions

Any impact of the recent emphasis in traditional SG research is likely to be felt principally in new electronic ceramic materials where thin layers are adequate, where cost is no bar to the use of expensive precursors, and where chemical purity and control of stoichiometry command a premium. The radical redirection of SSG research toward ultraheterogeneity has opened up different vistas for lowering ceramic reaction temperatures and controlling phases, microstructures, and morphologies by utilizing the unexpected phenomenon of solid-state epitaxy.

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