Researching both high- and low-temperature processing technologies, materials investigators are pursuing high-efficiency methods of synthesizing "perfect" ceramic powders. If prepared properly, such powders may be employed to produce defect-free structural and electronic components.

INTRODUCTION

Starting powder is, perhaps, the most critical factor in ceramics manufacture. Economical to produce, the "perfect" powder is pure and homogeneous, and features submicron, equiaxed particles with a narrow size distribution. With such powders, structural and electronic components can be made without defects. To achieve such qualities, industrial and academic researchers are currently exploring a variety of processing routes, including low-temperature methods (based on a chemical or colloidal approach) and high temperature technologies (involving vapor-phase or exothermic reactions).

Advantageously, most colloidal or chemical techniques are capable of producing powders at low temperatures, through calcining is usually required. These techniques range from sol gel (which includes the hydrolysis of metal alkoxides as well as precipitation and coprecipitation) to the evaporative decomposition of solids and the reductive dehalogenation of halides. Sol gel methods generally produce oxides for a wide range of electronic materials and are now being investigated for structural materials.

Sol gel processing involves particle growth from a liquid solution or colloidal suspension of colloidal silica, metallic acids or chlorides, and metal alkoxides \(\text{M(OR)}_{n}\), where \(R\) is an alkyl and \(M\) is a metal with valence \(n\). For metal alkoxides, the reaction involves several steps. The alkoxides mix because the \(\text{OR}\) groups provide solubility though alcohol may be necessary. Mixing is followed by hydrolysis where the OR groups become OH groups, resulting in chain-like or three-dimensional polymers. Hydrolysis rates are dependent on temperature, pH, and the concentrations of the starting materials.

All these parameters affect the final step of the reaction, which is polycondensation. At this stage, gelation occurs and an oxide is formed by oxygen bridging between two metal ions. The resulting material is dried into a monolithic, thin film or powder which is then sintered to full densification. Though sintering is needed, the sol gel method produces highly-reactive powders which require much lower temperatures. Another major advantage found in the hydrolysis of metal alkoxides is that precise control of the microstructure and homogeneity is possible, even with multicomponent systems.

NUCLEAR MATERIALS

A variation of sol gel technique is the sphere-cal process, developed at Oak Ridge National labs (ORNL). There, researchers used gel-derived urania and thoria microspheres as feed materials for fuel-pellet fabrication which is used in nuclear reactors and radioactive waste disposal. Droplet gelling occurs by the homogeneous release of ammonia when hexamethylenetetramine (HMTA) decomposes into 50-400 \(\mu\)m metal-oxide spheres. For radioactive waste disposal, \(\text{ZrO}_2\)-based spheres feature the highest waste loading (90%).

Also known as internal gelation (Figure 1), Oak Ridge technique has been extended to the preparation of a \(\text{ZrO}_2\)-toughened alumina with excellent homogenization to facilitate sintering. To avoid premature gelation in the feed system, long gelation times are usually required at low temperatures. Process conditions are dependent on the hydrolysis reactions and the solution chemistry of the gel's metal cations. Therefore, the process reagent concentrations of feed solutions and the conditions for gel sphere formation will be different for \(\text{Al}_2\text{O}_3\) and \(\text{ZrO}_2\) than for the nuclear materials.

Sol gel techniques are also being
developed for another nuclear application—tritium breeding materials for fusion reactors. These materials include: \( \text{Li}_2\text{O} \), \( \text{Li}_{2}\text{BeO}_2 \), \( \text{Li}_2\text{SiO}_3 \), \( \text{Li}_8\text{SiO}_5 \), \( \text{Li}_2\text{SiO}_3 \), \( \text{Li}_8\text{SiO}_5 \), \( \text{Li}_{2}\text{Be}_2\text{O}_5 \) and \( \text{Li}_{8}\text{SiO}_5 \). West Germany’s Institut für Material und Festkörperforschung III, has prepared \( \text{LiAI}_2\text{O}_3 \). West Germany's Institut für Material und Festkorperfors­chung III, has prepared \( \text{LiAI}_2\text{O}_3 \), \( \text{Li}_2\text{SiO}_3 \), \( \text{Li}_8\text{SiO}_5 \), \( \text{Li}_2\text{Be}_2\text{O}_5 \) and \( \text{Li}_{8}\text{SiO}_5 \) from aqueous solutions based on different types of alcohols. Doping of \( \text{Li}_2\text{SiO}_3 \) by \( \text{Al}^{3+} \) and \( \text{P}^{5+} \) has been accomplished with 90% sintered powder densities.

Scientists at the Chalk River Nuclear Laboratories in Canada have fabricated lithium aluminate pow­ders via the hydrolysis of equimolar mixtures of lithium and aluminum alkoxides. The type of aluminum alk­oxide determined the crystalline phase of the final material. At the University of Washington, researchers have prepared highly reactive lithium zir­conate with surface areas up to 190 m\(^2\)/g after calcining from mixtures of hydrated alumina and lithium hy­droxide.

**ELECTRONIC APPLICATIONS**

Wet-chemical preparation tech­niques have also been widely used for electronic applications. With piezo­electric and electrostrictive actuators, excellent properties have been ob­tained for materials based on the lead zirconate titanate (PZT) and lead magnesium niobate (PMN) systems. These latter materials are known as perovskite relaxor ferroelectrics and have excellent dielectric properties (K greater than 15,000) as well as a low firing capability (less than 1,000°C). More than 20 practical applications for electrostrictive actuators are un­der study, including deformable mirrors, cutting error compensation mechanisms, oil-pressure servovalves and surface-wave type piezomotors.

Martin Marietta researchers have used metal organic precursors to prepare a solid solution of lead zinc niobate-lead titanate near the mor­photropic phase boundary. After a va­riety of sintering tests, the amount of the perovskite phase formed and the density of material sintered from the gel-derived powder showed a sig­nificant improvement over conven­tionally processed material. At the Pennsylvania State University, where significant research is being conducted on the sol gel preparation of these and other materials, low temperature sinter­ing (1000 to 1260°C) achieved mi­crostructural homogeneity at 97% theoretical density for alkoxide hy­drolysis derived PZT powders.

Similar work at Alfred University involves a three-step process for making monozonized \( \text{Pb(S}_{0.57}\text{Sc}_{0.43})\text{O}_3 \) (PSN) powders. First, high-purity \( \text{Nb}_2\text{O}_5 \) powder, 0.5 to 0.6 \( \mu \)m in diameter, is made by the controlled hydrolysis of \( \text{Nb(O}C_2\text{H}_5)_n \). Next, a coating of \( \text{Pb} \) and \( \text{Sc} \) carbonates is grown on the particle surface, producing a wrinkled texture. The precursors are then calcined into oxides. Another study at Alfred involves doping PMN powders with zinc to shift the Curie temperature to room temperature, thus making the material more useful for multilayer capacitors. Battelle Columbus Labora­tories is also using wet chemical methods, based on a co-precipitation approach, to produce PMN.

Precipitation and coprecipitation methodology may be applied to other electronic materials, for applications ranging from transducers to varis­tors. For instance, Sandia National Laboratories has produced high-field \( \text{ZnO} \) varistors from the precipitation of precursor materials that have much lower sintering temperatures than conventional materials. To assure complete precipitation of dopant ions, the pH must be carefully controlled. In a two-step process, a hydrous oxide coprecipitate is induced by mixing solu­tions of \( \text{Co} \), \( \text{Mn} \) and \( \text{Zn} \) metal chlor­ides with \( \text{NaOH} \). The coprecipitate is then converted into a mixed oxide using oxalic acid. Such oxalate pow­ders can have particle diameters seven times smaller than directly precipi­tated oxalate powders.

Several oxide systems, important as piezoelectric materials, are being made by sol gel methods at several universities. At Alfred University, research­ers are investigating \( \text{Nb}_2\text{O}_5 \)-doped \( \text{BaTiO}_3 \). The alcohol dehydration of barium formate and citrate solutions of titanium and niobium yields a high purity, chemically homogeneous, finely-divided organic powder that decomposes during calcination to form a submicron, high-surface-area ce­ramic powder. Because it is easy to change the concentration of the do­pant and \( \text{Ba/Ti} \) ratios via sol gel, an optimal material may be obtained.

At Penn State, the piezoelectric material of interest is \( \text{PbTiO}_3 \), pre­pared from a mixed solution of lead nitrate and titanium tetrachloride. This forms an amorphous powder which is then calcined into the crys­talline state. The Penn State scien­tists are mixing this powder with...