2-2.2.3 Gel Routes

A few methods utilize the formation of a semi rigid gel or a highly viscous resin from liquid precursors as an intermediate step in the synthesis of ceramic powders, particularly for complex oxides when good chemical homogeneity is required.

The powder is commonly obtained by decomposing the gel or resin followed by milling and calcination to control the particle characteristics. In the formation of the gel or resin, mixing of the constituents occurs on the atomic scale by a polymerization process. Provided none of the constituents are volatilized during the decomposition and calcination steps, then the cation composition of the powder can be identical to that of the original solution. Hence these methods have the ability to achieve good chemical homogeneity. A drawback is that the decomposition product is commonly not in the form of a powder but consists of charred lumps. These lumps have to be ground and calcined to achieve the desired powder characteristics. Gel routes to ceramic powders are currently used mainly at the laboratory scale.

Sol–Gel Processing

The process is best applied to the formation of films and fibers and, with careful drying, to a few monolithic ceramics. Here, we would like to point out that the process, while expensive, can also be used for the production of powders. The procedure involves the formation of a polymeric gel by the hydrolysis, condensation, and gelation of a metal alkoxide solution, which is dried and ground to produce a powder. Carefully controlled drying is unnecessary in the production of a powder. Dried gels with lower viscosity are easier to grind, and the extent of contamination introduced during grinding is lower. Liquid removal under supercritical conditions produces almost no shrinkage so that a dried gel with low viscosity is obtained. Grinding can usually be carried out in plastic media. Powders with the stoichiometric mullite composition ($3Al_2O_3.2SiO_2$) produced by supercritical drying of gels have been shown to have fairly high sinterability.

The compacted powders sinter to nearly full density below ~1200°C, which is considerably better than mullite prepared by reaction of mixed powders. The sintering benefits are due to the amorphous structure and high surface area of the gel-derived powders. However, crystallization of the powder prior to compaction or sintering can severely reduce the sintering benefits.

The Pechini Method

The Pechini method refers to an original process for the preparation of titanates and niobates for the capacitor industry. The method has since been applied to many complex oxide compositions. Metal ions from starting materials such as carbonates, nitrates, and alkoxides are complexed in an aqueous solution with α-carboxylic acids such as citric acid. When heated with a polyhydroxy alcohol, such as ethylene glycol, polyesterification occurs, and on removal of the excess liquid, a transparent resin is formed. The resin is then heated to decompose the organic constituents, ground, and calcined to produce the powder. The typical steps in the method are illustrated in Figure 2.13 for the preparation of $SrTiO_3$ powders.

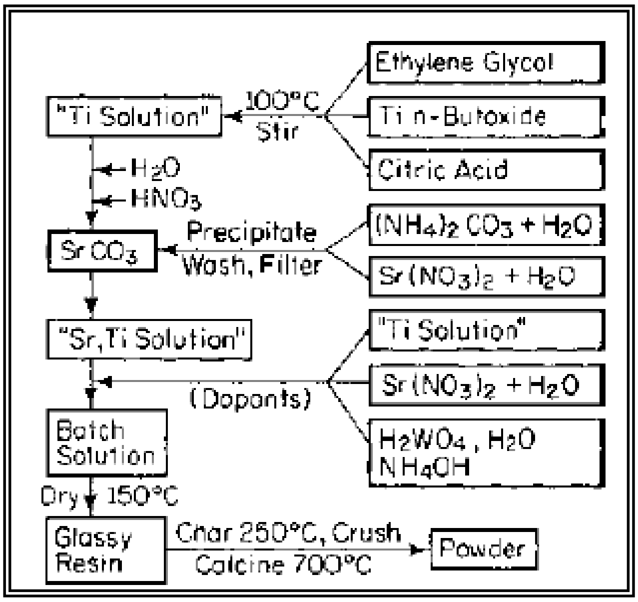

FIGURE 2.13 Flow chart for the preparation of strontium titanate powder by the Pechini method.

The Citrate Gel Method

The citrate gel method was can be illustrated by the synthesis of the ceramic superconductor $YBa_2Cu_3O_{7-x}$. Nitrate solutions of Y, Ba, and Cu were added to citric acid solution, and the pH was kept at ~6 to prevent precipitation of barium nitrate. Heating the solution at 75°C in air produced a viscous liquid containing polybasic chelate. Further heating at 85°C in a vacuum produced an amorphous solid that was pyrolyzed in air at 900°C to produce a crystalline powder.

The Glycine Nitrate Process

The glycine nitrate process is one of a general class of combustion methods for the preparation of ceramic powders. A highly viscous mass formed by evaporation of a solution of metal nitrates and glycine is ignited to produce the powder.

Glycine, an amino acid, forms complexes with the metal ions in solution which increases the solubility and prevents the precipitation of the metal ions as the water is evaporated. Good chemical homogeneity is therefore achieved, as outlined earlier. Glycine also serves another important function: it provides a fuel for the ignition step of the process since it is oxidized by the nitrate ions. The reactions occurring during ignition are highly explosive, and extreme care must be exercised during this step. Normally, only small quantities should be ignited at a time. Under well controlled conditions, a loose mass of very fine, crystalline powder (particle size less than a tens of nanometers) is obtained after ignition. When compared to the Pechini method, grinding and calcination of the product are not required. The very fine size and crystalline nature of the powder is believed to be a direct result of the short exposure to high temperatures during the ignition step. With adequate process control, the glycine nitrate process offers a relatively inexpensive route to the preparation of very fine, chemically homogeneous powders. It has been used for the preparation of simple oxides as well as complex oxides (e.g., manganites, chromites, ferrites, and oxide superconductors).