

## **Sol-gel technique: A veritable tool for crystal growth**

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### **ABSTRACT**

*This paper looks at the applications of sol-gel deposition technique to crystals growth. Sol gel technique which is one of the oldest methods of crystal growth is defined as a wet-chemical technique widely used in the fields of materials science and ceramic engineering. It is used primarily for the fabrication of materials starting from a colloidal solution (sol) that acts as the precursor for an integrated network or gel of either discrete particles or network polymers. It makes use of cheap and available materials. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine e.g., controlled drug release, reactive material and separation e.g., chromatography technology.*

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### **INTRODUCTION**

#### **1.1 SOL-GELL**

The methods of crystal growth can generally be grouped into two, thus; Vapour Phased Deposition which includes, Evaporation, Molecular Beam Epitaxy (MBE), Sputtering, Chemical Vapour Deposition(CVD) and Atomic Layer Deposition (ALD) and Liquid Based Growth which includes Chemical Solution Deposition, Electrochemical Deposition, Chemical Bath Deposition(CBD), Successive Ionic Layer Adsorption and Reaction (SILAR), Langmuir- blodgett films and Self Assembled Monolayers (SAM) and Sol gel method [1,2].

Crystals can be grown through any of the aforementioned methods. Our interest is on sol gel method. Sol-gel process is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. It is used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (*sol*) that acts as the precursor for an integrated network (or *gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions. In this chemical procedure, the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system containing both liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid or by the use of centrifugation to accelerate the process of phase separation.

Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing.

Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the

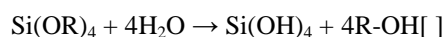
distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The precursor sol can either be deposited on a substrate to form a film (e.g., by dip coating or spin coating), cast into a suitable container with the desired shape (e.g., to obtain monolithic ceramics, glasses, fibers, membranes, aerogels), or used to synthesize powders (e.g., microspheres, nanospheres). The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (e.g., controlled drug release), reactive material and separation (e.g., chromatography) technology.

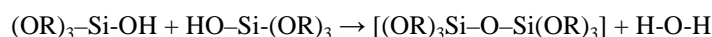
The interest in sol-gel processing started in the mid-1800s with the observation that the hydrolysis of tetraethyl orthosilicate (TEOS) under acidic conditions led to the formation of SiO<sub>2</sub> in the form of fibers and monoliths. Sol-gel research grew to be so important that in the 1990s more than 35,000 papers were published worldwide on the process [3-5, 6-8]. The discrete particles or continuous polymer network form the sol which evolves towards the formation of an inorganic network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution. Silicon tetraethoxide, or tetraethyl orthosilicate (TEOS) is a well studied alkoxide. The chemical formula for TEOS is given by: Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, or Si(OR)<sub>4</sub> where the alkyl group R = C<sub>2</sub>H<sub>5</sub>. Alkoxides react readily with water and as such is seen as ideal chemical precursors for sol-gel synthesis. It is called hydrolysis, because a hydroxyl ion becomes attached to the silicon atom as follows:



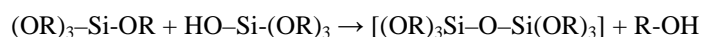
The amount of water and catalyst present determines whether hydrolysis may continue to completion, so that all of the OR groups are replaced by OH groups, as follows:



Complete hydrolysis of organometallics often requires a significant excess of water and/or the presence of hydrolysis catalysts such as acetic acid or hydrochloric acid. Intermediate species [(OR)<sub>2</sub>-Si-(OH)<sub>2</sub>] or [(OR)<sub>3</sub>-Si-(OH)] may result from partial hydrolysis reactions [9]. The two partially hydrolyzed molecules can link together in a condensation reaction to form a siloxane [Si-O-Si] bond:



or



Polymerization is associated with the formation of a 1, 2, or 3- dimensional network of siloxane [Si-O-Si] bonds accompanied by the production of H-O-H and R-O-H species. Condensation liberates a small molecule, such as water or alcohol. This type of reaction can continue to build larger and larger silicon-containing molecules by the process of polymerization. A polymer is a huge molecule (or macromolecule) formed from hundreds or thousands of units called monomers. The number of bonds that a monomer can form is called its functionality. Polymerization of silicon alkoxide, for instance, can lead to complex branching of the polymer, because a fully hydrolyzed monomer Si(OH)<sub>4</sub> is tetrafunctional (can branch or bond in 4 different directions). At low water concentration, under certain conditions, fewer than 4 of the OR or OH groups (ligands) will be capable of condensation, so relatively little branching will occur. The mechanisms of hydrolysis and condensation, and the factors that bias the structure towards linear or branched structures are the most critical issues of sol-gel science and technology. This reaction is favored in both basic and acidic conditions [10-17].

## 1.2 METHODS OF GEL PRODUCTION

There are four methods for the production of gels-

- (i) Flocculation of lyophilic- colloids by salts or precipitating liquids.
- (ii) Evaporation of certain colloidal solutions
- (iii) Chemical reactions that lead to change in shape of lyophilic molecules (e.g. the denaturation of albumen on heating involves some uncoiling of the protein molecules and a gel structure results).

(iv) Swelling of a dry colloid (xerogel) when placed in contact with a suitable liquid (e.g. starch granules added to water).

The presence of a network formed by the interlocking of particles of the gelling agent gives rise to the rigidity of a gel. The nature of the particles and the type of form that is responsible for the linkages determine the structure of the network and the property of the gel. Aerogels are sol-gel derived solid materials with porosities from about 80-98%. The high porosity is achieved through supercritical drying of wet gel in an autoclave [18, 19].

## 2.1 PROPERTIES OF GEL

There are about four properties of gel; swelling, syneresis, ageing and rheological properties.

(i) Swelling occurs if a xerogel is placed in contact with a liquid that solvates it, then an appreciable amount of the liquid is often taken up and the volume of the xerogel increases.

(ii) Syneresis occur when gels contract spontaneously and exude some of the fluid medium and the degree to which it occurs usually decreases as the concentration of the gelling agent increases.

(iii) Ageing occurs when colloidal system exhibit slow spontaneous aggregation. Ageing results in the gradual formation of a denser network of gelling agent.

(iv) Rheological properties occur when the gel exhibits mechanical properties of rigidity, tensile strength and elasticity that are characteristic of solids.

## 2.2 Applications of sol gel

### 2.2.1 Protective coatings

The applications for sol gel-derived products are numerous [20-25]. For example, scientists have used it to produce the world's lightest materials and also some of its toughest ceramics. One of the largest application areas is thin films, which can be produced on a piece of substrate by spin coating or dip coating. Protective and decorative coatings and electro-optic components can be applied to glass, metal and other types of substrates with these methods. Cast into a mold, and with further drying and heat-treatment, dense ceramic or glass articles with novel properties can be formed that cannot be created by any other method. Other coating methods include spraying, electrophoresis, inkjet printing or roll coating.

### 2.2.2 Thin films and fibers

If the viscosity of a sol is adjusted into a proper range, both optical and refractory ceramic fibers can be drawn which can be used for fiber optic sensors and thermal insulation, respectively. Many ceramic materials, both glassy and crystalline, have found use in various forms from bulk solid-state components to high surface area forms such as thin films, coatings and fibers [26, 27].

### 2.2.3 Nanoscale powders

In the process of precipitation, ultra-fine and uniform ceramic powders can be formed which are powders of single and multiple component compositions of nanoscale particle size for dental and biomedical applications. Composite powders have been patented for use as agrochemicals and herbicides. Powder abrasives, used in a variety of finishing operations, are made using a sol-gel type process. One of the more important applications of sol-gel processing is to carry out zeolite synthesis. Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicate sol formed by this method is very stable.

Sol gel is applied in research to entrap biomolecules for sensory (biosensors) or catalytic purposes, by physically or chemically preventing them from leaching out and, in the case of protein or chemically-linked small molecules, by shielding them from the external environment yet allowing small molecules to be monitored. The major disadvantages are that the change in local environment may alter the functionality of the protein or small molecule entrapped and that the synthesis step may damage the protein. To avoid this, various strategies have been explored, such as monomers with protein friendly groups (e.g. glycerol) and the inclusion of polymers which stabilize protein [28].

Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration, pervaporation and reverse osmosis. When the liquid in a wet gel is removed under a supercritical condition, a highly porous and extremely low density material called aerogel is obtained. On drying the gel by means of low temperature treatments (25-100 °C), it is possible to obtain porous solid matrices called xerogels. In 1950s, a sol-gel process was developed for the production of radioactive powders of UO<sub>2</sub> and ThO<sub>2</sub> for nuclear fuels, without generation of large quantities of dust.

### 2.2.4 Opto-mechanical

Sol gel route can be used to make macroscopic optical elements and active optical components as well as large area hot mirrors, cold mirrors, lenses and beam splitters all with optimal geometry at low cost. In the processing of high performance ceramic nanomaterials with superior opto-mechanical properties under adverse conditions, the size of the crystalline grains is determined largely by the size of the crystalline particles present in the raw material during the synthesis or formation of the object. Thus a reduction of the original particle size well below the wavelength of visible light ( $\sim 0.5 \mu\text{m}$  or 500 nm) eliminates much of the light scattering, resulting in a translucent or even transparent material.

Also, results indicated that microscopic pores in sintered ceramic nanomaterials, mainly trapped at the junctions of microcrystalline grains, cause light to scatter and prevented true transparency. It was also observed that the total volume fraction of these nanoscale pores (both intergranular and intragranular porosity) must be less than 1% for high-quality optical transmission. The density has to be 99.99% of the theoretical crystalline density [14, 15].

### CONCLUSION

In this work, sol gel deposition technique has been studied. It is used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (*sol*) that acts as the precursor for an integrated network (or *gel*) of either discrete particles or network of polymers. It makes use of cheap and available materials. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (e.g., controlled drug release), reactive material and separation (e.g., chromatography) technology. It is recommended that researchers develop more interest in the use of sol gel method in the growth of various thin films and crystals for enhanced output.

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