

Part 2:
Additional Developments

Section 6: Phosphor Synthesis

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Section 6

PHOSPHOR SYNTHESIS

6.1 Alternative Preparation Methods*

The traditional way of preparing phosphors has been by the mix and fire techniques detailed in the earlier sections. In this method, the reactants are mixed thoroughly either in dryness or in suspension; the mixture is then heated or fired under an appropriate atmosphere. To ensure the proper reactivity between the constituents of the phosphor, the reactants are generally granular with radii in the micrometer range. To further facilitate the reaction and to improve the crystallinity of the luminescent materials, flux agents or molten salts are often added to provide a more interactive medium for the reaction. The use of an interaction medium often results in lower reaction temperatures and allows for the optimization of the grain size of the luminophores being synthesized.

A suitable flux increases the reactivity of the constituents by dissolving at least one of the reactants and provides a medium to incubate the crystallization of the phosphor. There are two types of fluxes which are used, volatile and non-volatile. The volatile flux often reacts with the starting material and leaves the reaction mixture spontaneously, through either decomposition or evaporation. Commonly used fluxes include NH_4Cl , NH_4Br , AlF_3 , and boric acid. The amounts used are typically small, on the order of few mole percent. Molten salts are used as non-volatile fluxes and generally do not react with the starting materials. As the name denotes, these fluxes are always in the form of a melt. Large amounts of the salts are used (up to 30% by weight of the phosphor material); they generally do not leave the reaction mixture and must be removed by washing with water or other appropriate solvents. Examples of salts used for this purpose are Na_2MoO_4 , $\text{Na}_2\text{B}_4\text{O}_7$, Na_2SiO_3 , and $\text{Na}_4\text{P}_2\text{O}_7$.

Reactivity can also be improved by choosing starting materials which are unstable in controlled circumstances. Such reactants include the carbonates and the hydroxides which decompose with the emission of CO_2 or H_2O upon heating the mixture. This results in a more reactive mixture, as the interactive specific surface of the remaining elements increases in these processes.

A wet co-precipitation method is also being used. In these processes, the starting materials are dissolved in a solvent, come into contact with each other on an atomic or ionic level, and then co-precipitate forming an intimately commingled starting mixture. As an example, $\text{Y}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$ dissolved in water can be precipitated by the addition of a 2-to-1 solution of oxalic acid dissolved in hot water. The oxalates obtained in the precipitate can be converted to oxides by heating at a relatively low temperature of 800°C . Alternatively, the oxides can also be dissolved directly in hot diluted nitric acid to obtain a treatable precipitate. This method is used in cases in which an insoluble salt can be identified for each of the reaction constituents. Other routes for co-precipitation can involve sulfates or hydroxides.

The method of spray drying can also be used to synthesize luminescent materials. In this method, the reactants are first dissolved in a solvent, preferably water. Droplets of this solution are then injected into a gas stream and are heated as they are transported downstream. The steam heating results in a very fast evaporation of the solvent or water. As a result, an intimate reaction mixture is formed and deposited downstream from the flow.

The various methods described above pose the advantage of assuring a better and more homogeneous admixture of the reactants to be used in the synthesis and of generally requiring a lower temperature to achieve this synthesis.

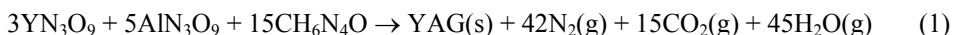
* The above section was kindly provided by Cees Ronda.

6.2 Combustion Synthesis of Phosphors*

Beginning in the late 1980's, combustion synthesis has been investigated as a method to produce homogeneous, crystalline, fine oxide powders, as an alternative to time-consuming solid-state reaction and sol-gel processing techniques.¹⁻³ The method produces rapid, exothermic, self-sustaining reactions resulting from the appropriate combination of oxidizers (e.g., metal nitrates, ammonium nitrate, or ammonium perchlorate) and an organic fuel (e.g., urea, carbonylhydrazide, or glycine). For combustion to occur, it is necessary that a large amount of heat be released during the formation of the products. The reaction of aluminum nitrate, $\text{Al}(\text{NO}_3)_3$, and carbonylhydrazide, $\text{CH}_6\text{N}_4\text{O}$, to form aluminum oxide, Al_2O_3 , is an example of a highly exothermic reaction, having a negative enthalpy of reaction ($\Delta H_{\text{rxn}} = -3800 \text{ kJ/mol}$).

Later in the mid-1990's, several research groups began to investigate the use of combustion synthesis for oxide phosphor preparation⁴⁻⁶ and found it to be a technique of interest for phosphor synthesis in general. For oxide phosphors, the advantages of combustion synthesis are in its ability to produce well-crystallized, fine particle size powders rapidly without extensive high temperature ($\geq 1500^\circ\text{C}$) annealing and mechanical separation (e.g., grinding and milling) steps. Grinding has often been implicated in the degradation of luminescent emission intensity through the creation of surface defects that quench the luminescence.

A composition of metal nitrates and fuel in which the fuel reacts completely with all of the metal nitrates in the mixture, so that no residues remain in the product material, is known as a stoichiometric ratio or composition. Equation 1 is an example of a stoichiometric combustion reaction of yttrium nitrate, aluminum nitrate, and carbonylhydrazide to form yttrium aluminum garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG).



When complete combustion occurs, the only gaseous products, N_2 , CO_2 , and H_2O , are released and no residuals are left in the synthesized YAG material.

The stoichiometry of metal nitrate-fuel mixtures is expressed in terms of the elemental stoichiometric coefficient, Φ_e , that is the ratio of the oxidizing to reducing components of the metal nitrate-fuel precursor mixture and is defined as:

$$\Phi_e = \frac{\sum(\text{coefficient of oxidizing elements in specific formula}) \times \text{valency}}{(-1) \sum(\text{coefficient of reducing elements in specific formula}) \times \text{valency}} \quad (2)$$

*This section was kindly provided by L.S. Rohwer.

The coefficients of the oxidizing and reducing elements are obtained from the balanced chemical equation for the combustion reaction of metal nitrates and a fuel, as noted below. The mixture is stoichiometric when $\Phi_e = 1$; it is fuel lean when $\Phi_e > 1$, and fuel rich when $\Phi_e < 1$. Stoichiometric mixtures are reported to produce maximum energy.

The oxidizer/fuel molar ratio required for a stoichiometric mixture ($\Phi_e = 1$) is determined by summing the total oxidizing and reducing valencies in the oxidizer compounds and dividing by the sum of the total oxidizing and reducing valencies in the fuel compounds. In these calculations, oxygen is considered to be the only oxidizing element and has a positive valence while carbon, hydrogen, and metal cations are considered to be reducing elements and have a negative valence. Nitrogen is considered to be neutral. For example, in Equation 1, $Y(NO_3)_3$ and $Al(NO_3)_3$ are oxidizers and the reducing agent is CH_6N_4O . For $Y_3Al_5O_{12}$ synthesized using carbohydrazide fuel, the metal nitrate to carbohydrazide molar ratio is given by:

$$\frac{\frac{3}{8} [1 Y \times (-3)] + [3 N \times 0] + [9 O \times 2]}{(-1) \times \{[1 C \times (-4)] + [6 H \times (-1)] + [4 N \times 0] + [1 O \times 2]\}} + \frac{5}{8} \frac{\{[1 Al \times (-3)] + [3 N \times 0] + [9 O \times 2]\}}{8} = \frac{15}{8} = 1.875 \quad (3)$$

Thus, the metal nitrate to carbohydrazide molar ratio = 1.875 is needed to obtain $\Phi_e = 1$ and complete combustion of all components.

Combustion reactions are initiated in a muffle furnace or on a hot plate at temperatures of 500°C or less; these temperatures are clearly much lower than the temperature at which crystallization of the desired phase takes place during conventional processing. In a typical reaction, the precursor mixture of de-ionized water, metal nitrates, and fuel boils, dehydrates, decomposes, and ruptures into a flame after about 3–5 minutes. The resultant product appears as a porous foam. The chemical energy released during the exothermic reaction between the metal nitrates and fuel can rapidly heat the system to a high temperature (>1800°C) and sustain that high temperature in the absence of an external heat source. Thus, the target phase(s) can be achieved with significantly reduced external energy input.

The type of fuel and the fuel to oxidizer ratio affect the adiabatic flame temperature, T_f . The fuel alters the energetics and exothermicity of the reaction, and provides a method to increase or decrease the adiabatic flame temperature. The flame temperature can also be increased by adding excess oxidizer such as ammonium nitrate, or by adjusting the fuel to oxidizer molar ratio so $\Phi_e = 1$. Hess' law can be used to approximate the adiabatic flame temperature for a combustion reaction:

$$T_f = T_o + \frac{\Delta H_r - \Delta H_p}{C_p} \quad (4)$$

where ΔH_r and ΔH_p are the enthalpies of formation of the reactants and products, respectively, and C_p is the heat capacity of products at constant pressure.

Powders obtained from combustion reactions with urea or carbohydrazide fuels are luminescent in the as-synthesized state. Combustion reactions using glycine fuel yield amorphous powders or ash which must be annealed to produce crystalline luminescent powders. The photoluminescence emission spectra of YAG:Cr phosphors produced with carbohydrazide, urea, and glycine fuels followed by a heat treatment in air at 1300°C for 1 hour show the effect of flame temperature on the luminescent properties. The maximum

flame temperatures during reactions with carbohydrazide, urea, and glycine were 1825, 1780, and 1210°C, respectively. The photoluminescence intensity increases for powders obtained from reactions that reached higher flame temperatures. This is an indication that certain properties of the resulting powders, such as crystallite size or and degree of disorder of the local environment at the activator ions, are affected by the flame temperature of the reaction.

The flame temperature is also controlled by the fuel to oxidizer ratio of the particular fuel used. The integrated photoluminescence intensity is a maximum for reactions at or near stoichiometry.

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6.3 Preparation of Phosphors by Sol–Gel Techniques*

6.3.1 Introduction

Phosphors used for most emissive display devices are in the form of powders. The quality of the displays depends on the nature of the powders used; fine and uniform powders with good crystallinity are generally preferred. This is especially true in low-voltage applications such as in the field emission displays of current interest. In these devices, lower energy electrons do not penetrate into phosphor grains very deeply, and in order to maintain efficiency the size of phosphor grains has to be reduced to reflect this fact. The grain size of phosphors prepared via solid-state chemical reactions depends on the temperature and the length of the sintering process. Lower temperature and shorter sintering periods give rise to smaller grain size particles, but both the crystallinity and grain uniformity are poor if the treatment parameters are such as not to allow the chemical reaction to be completed.

To resolve this problem, wet methods of preparation are often used; in the wet method, aqueous solutions of specific constituent metallic salts are employed. The addition of a $\text{NH}_4(\text{OH})$ or oxalic acid causes the metallic hydroxides or oxalates to precipitate from the mixture; in these cases, the ingredients of the precipitate are in contact with each other at a molecular level and an efficient chemical reaction normally occurs.

*This section was kindly provided by W. Jia.

The sol-gel method of phosphor preparation is regarded as a wet method. A kind of metal-organic compounds, known as alkoxides of metals, is used as precursors. These metal-organic alkoxides either are in liquid form or are soluble in certain organic solvents. Through the use of the appropriate reagents, the processes hydrolysis and gelation can be induced to produce homogeneous gels from the mixture of alkoxides. To obtain powder or ceramic samples, the gels can be baked, sintered, and powderized as in other traditional methods. The sol-gel method is advantageous inasmuch as thin films or coatings of the phosphor can be formed on substrates directly and/or the sol-gel can be molded into designated forms.

The sol-gel technique presents the following advantages:

- (a) High homogeneity of the chemical composition of the materials produced occurs. Molecule-level-homogeneous multi-component materials can be obtained. Because of the better homogeneity, contributions to the optical spectra of these materials from inhomogeneous sources are generally expected to be smaller than those encountered in unordered systems.
- (b) High uniformity of doping ions distribution exists. No "local" concentration quenching will occur because of impurity clustering, and higher doping concentration becomes possible.
- (c) Processing temperature can be very low. This allows the doping of fragile organic and biological molecules into porous inorganic materials and the fabrication of organic-inorganic hybrid materials.
- (d) The microstructure (porosity and size of pores) of the materials can be controlled. Nano-scale uniform pores can be obtained at intermediate processing temperature while high-density materials can be produced with higher annealing temperature.
- (e) Thin films and multi-layers coatings of sol-gel materials can be readily prepared by spinning or dipping methods during the gelation period.
- (f) The sol-gel procedures produce little unintentional contamination. No milling and grinding are needed; for example, processes are known to contaminate samples. Fluxes, such as B_2O_3 , H_3BO_3 , and NH_4Cl , which are commonly used in ceramic technology and contaminate the end products, are no longer needed. In cases where phosphor powders are prepared by the sol-gel method, powderizing may be used and trace of foreign particles can be mix in. This "contamination" does not enter into the lattice and will not affect the intrinsic optical properties of the phosphor.

The technique has the following disadvantages:

- 1. The drying and annealing processes have to be slow and deliberate; otherwise cracks and striations will appear in the samples.
- 2. It is difficult to completely remove the residual hydroxyls from the sol-gel materials. To get rid of these organic groups, samples have to be annealed above $1000^{\circ}C$ and this may produce undesirable side effects.

The sol-gel method has been widely used to prepare a number of phosphors¹⁰⁻¹² for displays and other materials that are of technical importance. For example, Willi Lehmann reported in 1975 that very efficient luminescence was observed in, what he called, heterogeneous materials, such as $SiO_2:CaX_2-Eu^{2+}/Mn^{2+}$ (where $X = Cl, Br, \text{ or } I$), prepared by a solid-state reaction.¹³ These materials are similar to those found in the nanoclusters in SiO_2 which have been developed recently via the sol-gel method described in the first section.¹⁴⁻¹⁷ There are two ways to prepare such nanophosphor composites: (a) Alkoxide solutions of the phosphor are prepared from the appropriate precursors and then blended into the sol of SiO_2 (or other matrixes); the gelation process then proceeds as before. (b) Nanophases can be obtained by phase aggregation from doped SiO_2 or other matrices during thermal treatments. Different

nanophosphor embedded glasses have been fabricated with this method. These materials are transparent and can be used for displays and laser devices.^{18,19}

6.3.2 Sol-gel techniques

The sol-gel method is a chemical technique that uses metal alkoxides for the synthesis and production of glasses or ceramics through a series of chemical processes, including hydrolysis, gelation, drying, and thermal treatment. The sol-gel technique was developed as early as 1864; T. Graham¹ prepared gels of silica from aqueous salts, while M. Ebelmen² obtained silica gels from metal alkoxides. The potential of the sol-gel process was not appreciated until 1980, when it was "rediscovered" and found to be very useful in synthesizing various materials of practical importance, such as optical glasses and solid-state laser materials. Since then the method has received considerable attention and has been investigated extensively.³

In general, a sol is defined as a colloid of solid particles suspended in a liquid; the particles consist of dense oxide or polymetric clusters formed by the precursors and reagents. A gel, on the other hand, is a composite substance consisting of a continuous solid skeletal structure which results from the gelation of the sol; the gel forms cells which encapsulate colloidal liquids. This solute can be driven from the gel through thermal treatment, and a solid glass or ceramic is produced in this way. As an example, the procedure for the preparation of doped SiO₂ sol-gel glasses is described; similar procedures are applicable to other oxide compounds.

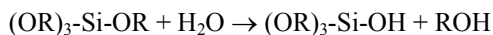
1. Preparation of precursor solutions

The initial raw materials for sol-gel preparations consist of metal alkoxides either in solid or in liquid form (Table 1); an alkoxide is a metalorganic compound, in which a hydrogen atom belonging to the hydroxyl (OH) group on an alcohol is replaced by a metal atom. Since the sol-gel method is a wet chemical method, a proper solvent is needed to convert solid alkoxides, if used, into liquid form. Some alkoxide solutions are commercially available (see Table 1). Doping or activator ions are introduced through either using another alkoxide solution or an aqueous solution of the doping ions. These liquid mixtures of the metal alkoxides are stirred for an extended period, on the order of several hours. To stimulate hydrolysis, a mixture of water to alcohol to HCl with pH ~2–5 is added.

Because the chemical-physical processes involved are similar for all metal alkoxides, we use silicon alkoxides as an illustrative example for the preparation of sol-gel materials, silicate-related materials in this case. For these matrices, TMOS (tetramethoxysilane, Si(OCH₃)₄, liquid) or TEOS (tetraethoxysilane, Si(OC₂H₅)₄, liquid) are commonly used. They react readily but are not soluble in water; a solvent such as MeOH (methanol) or EtOH (ethanol) is normally used to produce the precursor solution.

2. Hydrolysis^{3,4}

A mixture of water, alcohol, and hydrochloric acid (HCl) is prepared so that it has a pH in the range of 2–5; HCl acts as a catalyst in this process. This acidic solution is added slowly (dropwise) into the precursor alkoxide mixture. The reaction of alkoxides with water is called hydrolysis; in hydrolysis, a hydroxyl (OH) group attaches itself to the metal atom by replacing the alkoxide group (OR) in the TMOS or TEOS. A typical reaction goes as:



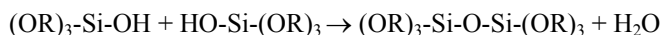
Here R stands for the alkyl (alkylic radical), C_nH_{2n+1} ; $R=CH_3$ for TMOS; and $R=C_2H_5$ for TEOS. Hydrolysis can occur with any one of the (OR) groups of the molecule. If the sol-gels are to be doped, an aqueous solution containing the doping ion/ions is also blended in during the hydrolysis step.

Table 1. Commonly used metal alkoxides and recommended solvents for solids

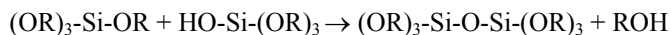
Name	Chemical Formula	Solvents
aluminum isopropoxide	$Al(OC_3H_7^i)_3$	isopropanol
aluminum <i>n</i> -butoxide	$Al(OC_4H_9^n)_3$	<i>n</i> -butanol
aluminum <i>sec</i> -butoxide	$Al(OC_4H_9^s)_3$	liquid
barium ethoxide	$Ba(OC_2H_5)_2$	ethanol
barium isopropoxide	$Ba(OC_3H_7^i)_3$	isopropanol
bismuth isopropoxide	$Bi(OC_3H_7^i)_3$	isopropanol
calcium ethoxide	$Ca(OC_2H_5)_2$	ethanol
calcium methoxide	$Ca(OCH_3)_2$	methanol
cerium isopropoxide	$Ce(OC_3H_7^i)_3$	isopropanol
copper ethoxide	$Cu(OC_2H_5)_2$	ethanol
dysprosium isopropoxide	$Dy(OC_3H_7^i)_3$	toluene-isopropanol
erbium isopropoxide	$Er(OC_3H_7^i)_3$	toluene-isopropanol
gadolinium isopropoxide	$Gd(OC_3H_7^i)_3$	toluene-isopropanol
gallium isopropoxide	$Ga(OC_3H_7^i)_3$	liquid
germanium methoxide	$Ge(OCH_3)_4$	liquid
germanium ethoxide	$Ge(OC_2H_5)_4$	liquid
germanium isopropoxide	$Ge(OC_3H_7^i)_4$	liquid
lanthanum isopropoxide	$La(OC_3H_7^i)_3$	isopropanol
lead isopropoxide	$Pb(OC_3H_7^i)_2$	isopropanol
magnesium methoxide	$Mg(OCH_3)_2$	methanol
magnesium ethoxide	$Mg(OC_2H_5)_2$	ethanol
manganese isopropoxide	$Mn(OC_3H_7^i)_2$	isopropanol
praseodymium isopropoxide	$Pr(OC_3H_7^i)_3$	toluene-isopropanol
tetraethoxysilane (TEOS)	$Si(OC_2H_5)_4$	liquid
tetramethoxysilane (TMOS)	$Si(OCH_3)_4$	liquid
strontium isopropoxide	$Sr(OC_3H_7^i)_2$	isopropanol
titanium(iv) ethoxide	$Ti(OC_2H_5)_4$	liquid
titanium(iv) methoxide	$Ti(OCH_3)_4$	methanol
titanium(iv) isopropoxide	$Ti(OC_3H_7^i)_4$	liquid
tungsten(vi) ethoxide	$W(OC_2H_5)_6$	ethanol
tungsten(vi) isopropoxide	$W(OC_3H_7^i)_6$	isopropanol
yttrium isopropoxide	$Y(OC_3H_7^i)_3$	isopropanol
zinc isopropoxide	$Zn(OC_3H_7^i)_2$	isopropanol
zirconium <i>n</i> -propoxide	$Zr(OC_3H_7^n)_4$	<i>n</i> -propanol
zirconium <i>n</i> -butoxide	$Zr(OC_4H_9^n)_4$	<i>n</i> -butanol

3. Gelation ^{3,4}

With the proper thermodynamic conditions, gelation occurs. Gelation is a continuous process in which two partially hydrolyzed molecules begin to connect and intertwine with each other with the release (condensation) of water when in a water solution:



Alcohol, ROH, is released when an alcohol solution is employed:



ROH is an alcohol: ROH=C₂H₅OH for TEOS and CH₃OH for TMOS.

With continuing gelation, larger structures are produced by polymerization; chains of polymers can cross-link to form three-dimensional clusters. Small clusters suspended in the liquid constitute the sol. Through the gelation process, these clusters begin to grow by combining with monomers or other clusters while releasing or condensing water or alcohols. Different metal alkoxides can also coalesce to form "compound" clusters.

Several factors affect the rate of sol and gel formation including the temperature; the relative concentration of the alkoxide precursors, water, and solvent; and the pH of the total admixture. In most cases, sol-gel synthesis is carried out at room temperature, though both the sol and gel formation rates are known to increase with increasing temperature. Because water and alkoxysilanes are immiscible, a common solvent such as alcohol is also normally used as a homogenizing agent.

In our example, silica gels prepared at low pH (<3) and low water content (less than 4 mol% water per mole of alkoxide) produce primarily linear polymers with low cross-link density. Additional cross-links form during gelation and the polymer chains become increasingly entangled. Silica gels prepared under more normal condition (pH ≈5–7) and/or higher water contents produce highly branched clusters which behave as discrete species; these clusters link together during gelation. At still higher pH and excess water content, colloidal silica is formed. Links between clusters keep on multiplying until a giant cluster forms that spans the vessel; during gelation, the viscosity and the elastic modulus of the solution increase rapidly. The final spanning cluster forms a skeletal framework which encloses cells containing the liquid phase (water or alcohol) and defines the gel phase. The solid network retards the escape of the liquid and prevents structural collapse.

4. Aging and drying

Aging leads to changes in the structure and other properties of the gel. That is through further condensation, dissolution, and re-precipitation of monomers or oligomers. Syneresis or spontaneous shrinkage of the network of the gel takes place as bond formation or attraction between clusters induces a contraction of the network and expulsion of liquid from the pores.

Drying by evaporation under normal conditions gives rise to pressure within the pores that causes shrinkage of the gel network. Pressure gradients develop through the volume of the gels, so that the networks are compressed more at the surfaces than in the bulk. If the gradients are too large, this may cause cracking of the sample.

After shrinkage stops, further evaporation drives the meniscus of the liquids into the bulk and the rate of evaporation decreases. The resulting dried gel is called a xerogel. Xerogels are useful in the preparation of dense ceramics and are also interesting because of their high porosity and large surface area; these materials are useful as phosphors, catalytic substrates, filters, and vapor sensors.^{5,6}

5. Annealing and porosity control

Additional treatment of the sol–gel is required to produce pore-free ceramic materials; sintering at high temperatures results in densification driven by interfacial energy considerations. By heating, the gel constituents move by viscous flow or diffusion in such a way as to reduce the solid–vapor interfacial areas and hence reduce porosity. Removal of organics takes place by endothermic carbonization near 200°C, followed by exothermic oxidation at temperatures between 300 and 400°C. For the silicate system of our example, the exothermic process is suppressed if the gels are heated under inert conditions, where oxidation is prevented. The temperature interval 400–525°C represents a region where considerable skeletal densification occurs with little associated weight loss. Structural relaxation, a process by which free excess volume is removed by diffusive motion of the network, is the predominant shrinkage mechanism in this temperature interval. The condensation (water or alcohol) and pyrolysis reactions that occur during heating liberate a large volume of gas that can generate high pressures. Because of low permeability of the small pores in the network, this may cause cracking when the samples are heated between room temperature and 400°C. At 800°C, there is partial densification of the sol–gel; by 900°C, the gel is completely densified leaving only a trace of silanols (Si–OH).

6. Techniques for other materials

Techniques to prepare other oxide and nitride compounds are similar to those used for SiO₂.⁶ As an example, to make Al₂O₃, Al(OC₄H₉)₃ (see Table 1) can be used. Hydrolysis can be conducted at 80°C with 1 mol of aluminum *sec*-butoxide, 100 mol of H₂O, and 0.07 mol of HCl. Alumina sols, then wet gels, and then dried gels can be obtained through the procedures of hydrolysis, gelation, and drying, as described above.⁷ Monolithic transparent γ -alumina results when an annealing temperature of 500°C is used; the alumina becomes α -phase when annealed at 1200°C.⁷

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