

Review article

Recent advances in sol–gel synthesis of monolithic silica and silica-based glasses

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ABSTRACT

Studies on sol–gel synthesis of monolithic silica and silicate glasses are summarized. Major research efforts have been devoted to avoid the fracture problems, associated with the extensive shrinkage of wet gels during drying. Supercritical drying, incorporation of silica fillers, and reduction of the surface tension of pore liquid have been used to form monolithic dried gels without fracture. More recent studies have shown that wet gels derived from alkoxides can be dried in a relatively short time without fracture at ambient pressure, by employing controlled drying accompanied by the cavitation of the pore liquid, macroscopic phase separation in parallel with gelation, and fluorine modification. By optimizing the synthesis procedure, it is also possible to reduce the use of reagents such as external alcohols, organic solvents, and other additives, which are removed during synthesis and are unnecessary in the final products. Another subject of considerable interest is the development of silica-based functional glasses that are difficult to form by conventional melt–quench and vapor–phase methods, by taking advantage of melt-free processes conducted at relatively low temperatures. Most of the recent studies on the functionalization of sol–gel-derived silica glasses are concerned with the doping of nanoparticles, rare earth ions, and/or fluorine.

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1. Introduction

Sol–gel method is an important wet-chemical technique used to synthesize inorganic materials and organic–inorganic hybrids from liquid sources. Among the various compositions explored in sol–gel synthesis, silicate systems have been studied most extensively because molecular silicon sources with moderate reactivities (e.g., tetraalkoxysilanes) are readily available. The hydrolysis and polycondensation of tetraalkoxysilanes yield silica gels, which can be converted into silica glasses at relatively low temperatures (~ 1000 – 1500 °C) without melting. This melt-free process is attractive for the development of glasses that would be difficult to realize by conventional melt-quench and vapor phase methods, because it has the potential to increase the concentration of dopants, expand the compositional range, and construct tailored photo- and magnetoactive centers. However, sol–gel-derived wet gels are easily fractured during drying, making it difficult to obtain monolithic dried gels suitable as the precursors of silica glasses. Thus, the sol–gel synthesis of monolithic silica glasses and silica-based functional glasses remains a major challenge.

This review is intended to provide a brief overview of the current status of the sol–gel syntheses of dense monolithic silica and silicate glasses, with a focus on glasses and glass-ceramics with good optical transparency. Sol–gel-derived monolithic polycrystalline ceramics, porous monoliths, thin films, particles, and organic–inorganic hybrids fall outside of the scope of this paper. Studies prior to 2000 have been covered more extensively by several excellent books [1,2] and review articles [3–9]. Recent advances and selected topics in this field will be highlighted.

2. Synthesis of monolithic precursor gels

2.1. General approach

The principal difficulty in the sol–gel synthesis of monolithic dried gels is fracture during drying. This is mainly because of the stress arising from the large degree of shrinkage, which is attributed to the small volume fraction of the silica component in the precursor solution. For example, simple calculations using densities and formula weights indicate that the volume of silica glass is ~ 0.18 and ~ 0.12 of those of tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), respectively, for the same number of silicon atoms. Further, the addition of water and cosolvents to precursor solutions increases the actual volume change. Fig. 1 shows an example of the volume difference between a wet gel, a dried gel, and a glass.

The driving force for the shrinkage is the evaporation of solvent. As the drying proceeds, liquid–vapor interfaces enter into wet gels, and capillary pressure is induced at the menisci. For a cylindrical pore with a radius of r , the capillary pressure P_c is expressed by [2,6,8,9]

$$P_c = -\frac{2\gamma_{LV} \cos \theta}{r} \quad (1)$$

$$= -\frac{2(\gamma_{SV} - \gamma_{SL})}{r}, \quad (2)$$

where θ is the contact angle, and γ_{LV} , γ_{SV} , and γ_{SL} , respectively, denote the interfacial tensions between the liquid and the vapor, the solid and the vapor, and the solid and the liquid. γ_{LV} is also referred to as the surface tension of the liquid. The negative sign indicates that the liquid is in tension.

On the basis of Eq. (1), general principles to suppress fracture have been established [2,6,8,9]. Table 1 summarizes the effects of various known methods to avoid and suppress the fracture problem. Methods to decrease γ_{LV} and increase r have been well studied and will be described in detail later in this section. Methods to

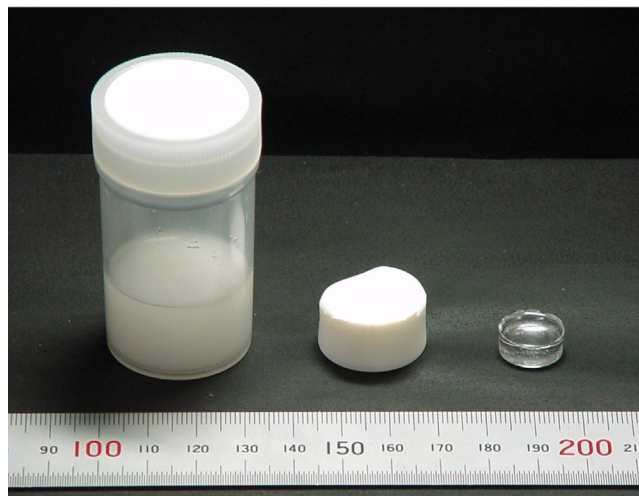


Fig. 1. Comparison of the sizes of a wet gel, dried gel, and glass prepared from 25 mmol (5.2 g) of tetraethoxysilane (TEOS) following the procedure described in Ref. [57]. The overall TEOS:H₂O:HNO₃:ammonium acetate molar ratio of the solution is 1:10:0.002:0.02.

increase θ , which corresponds to a decrease in $\gamma_{SV} - \gamma_{SL}$ (Eq. (2)), are less common. Modification of the surfaces of wet gels with alkyl groups by silane coupling agents renders the gel surfaces hydrophobic, and has been used to form low-density monolithic xerogels under ambient pressure conditions [10]. Another example of the formation of hydrophobic surfaces is observed in HF-catalyzed gels, which will be described in Section 4. Gels prepared from organoalkoxysilanes are soft and hydrophobic [11,12], and may be used as precursors for monolithic silica glasses, although the organic substituents must be combusted during sintering to avoid carbonization. When silicon alkoxides are hydrolyzed in the presence of acid catalysts, rather flexible siloxane polymers of low fractal dimensions are formed, which results in dense and relatively transparent silica gels with small pore sizes and volumes. These can be sintered at lower temperatures than the gels with larger pores [13]. However, before the completion of the sintering, water molecules originating from the condensation of adjacent SiOH groups must be released to avoid explosion and bloating (forming) [14–16]. Slow drying is commonly used to suppress inhomogeneous shrinkage during drying and reduce the stress that leads to fracture. It has also been reported that slow drying decreases the bulk density and increases the pore size and volume [15]. These phenomena may also contribute to the suppression of fracture during slow drying.

A practical method for decreasing γ_{LV} is to incorporate additives that lowers the γ_{LV} of the solvent phase. The vapor pressure of the additive should be less than that of water, which is essential for hydrolysis but has a large γ_{LV} (~ 72 mN m⁻¹ at 25 °C). Surfactants can be used to decrease γ_{LV} and suppress fracture [6]. Other types of additives include organic solvents with low γ_{LV} and high boiling points (T_{bp}); these are often termed “drying control chemical additives” (DCCAs). Formamide ($T_{bp} = 210$ °C, $\gamma_{LV} \simeq 57$ mN m⁻¹ at 25 °C) has been used as a DCCA to prepare monolithic dried gels [17]. However, the conversion of these gels into silica glass is likely to be difficult because the residual formamide leads to the fragmentation of gels at ~ 300 °C [17]. Subsequently, *N,N*-dimethylformamide (DMF, $T_{bp} = 153$ °C, $\gamma_{LV} \simeq 36$ mN m⁻¹ at 25 °C) has proven to be a better DCCA, because drying at ~ 150 °C yields DMF-free monolithic gels with large pores, which are readily sintered to silica glasses [18]. The differences in the chemical properties and effects between formamide and DMF in the sol–gel processing of silica gels

Table 1
Methods to avoid fracture during drying.

Methods	Effects				
	Decrease in P_c			Increase in strength	Reduction in stress
	Decrease in γ_{LV}	Increase in r	Decrease in θ		
Addition of DCCA and/or surfactant	○				
Supercritical drying	○				
Base catalysis		○		○	
Aging		○		○	
Incorporation of silica particles		○		○	
Macroscopic phase separation		○			
HF catalysis		○	○		
Modification with alkyltrialkoxysilanes			○		○
Acid (except for HF) catalysis					○
Slow drying					○

have been discussed [19–21]. The presence of two methyl groups in DMF lowers the surface tension and partially destroys the hydrogen bond network in the solvent. The lower surface tension facilitates drying without fracture, and the destruction of the hydrogen bond network may be favorable for the removal of DCCA during drying.

A reduction of γ_{LV} is realized in a distinctive manner in supercritical drying [22,23], which utilizes the fact that the liquid–vapor interface disappears above the critical temperature and critical pressure of the pore liquid. Because of the absence of capillary pressure, shrinkage during drying is small, and highly porous gels, commonly termed “aerogels,” are obtained without fracture [6]. Observations indicate that supercritical conditions are not always necessary to obtain aerogels that exhibit small linear drying shrinkage [24]. The shrinkage is suppressed significantly above a subcritical pressure threshold, suggesting that the gel strength overcomes the capillary pressure above the threshold [24].

Another way to reduce P_c is to increase r . Base-catalyzed gels, which possess average pore sizes that are generally larger than those of acid-catalyzed gels, have been preferentially used as precursors to form monolithic glasses [13,14,25,26]. This is mainly because the silica oligomers formed by base catalysis are larger and more rigid than those formed by acid catalysis [13,27,28]. The shrinkage of the base-catalyzed gels during drying is smaller than that of the acid-catalyzed gels, which also contributes to the large pore size and volume. The large porosity of the base-catalyzed gels can be typically seen in Tables 2 and 3 for gels prepared using different catalysts at a TEOS:EtOH:H₂O:catalyst molar ratio of 1:4:4:0.05 [29]. With base catalysis, inhomogeneous phase separation and precipitation often take place in precursor solutions. However, these can be suppressed by partially hydrolyzing alkoxy groups prior to the base hydrolysis (i.e., a two-step acid–base hydrolysis procedure [30]).

The pore size of the base-catalyzed gels can be further increased by aging, because the solvent is basic and the solubility and dissolution rate of silica in water are high at high pH [2,31]. The coarsening

of the gel framework by dissolution and reprecipitation (ripening) is enhanced at high temperatures [32,33]. Aging usually strengthens the gel framework [2], and this phenomenon is also beneficial in suppressing the fracture during drying as well as bloating during sintering [14]. It has been reported that alcoholic solutions of alkoxides are useful as soaking solutions, because they provide new monomers and strengthen gels during aging, resulting in a reduction of the probability of fracture during drying [34].

Silica particles such as fumed silica and colloidal silica have been frequently incorporated into precursor solutions to obtain monolithic silica gels and glasses. At the interstices of the silica particles, macropores that reduce the capillary pressure are formed [35]. Zeolite particles have an additional advantage in that metallic ions in the zeolites are incorporated simultaneously [36]. Silica particles smaller than 1 μm are typically used to complete sintering while avoiding the crystallization problem [9]. These silica particles also strengthen the gel body, facilitating drying while avoiding fracture. Typical sintering temperatures for such silica particles are 1400–1500 °C [9,37–39]. However, the temperature can be lowered to 1200–1350 °C by embedding silica particles in gels derived from silicon alkoxides [40,41]. These techniques have been utilized to form large monoliths [37,38,40], glasses with complex shapes [35], glass tubes [42,41], and photomask substrates for excimer laser photolithography [43].

Although an increase in r is a general approach for obtaining monolithic dried gels, as described above and later in Section 2.2, it is noteworthy that gels with small pores can also be dried without fracture by an anomalous mechanism that does not follow the principles derived from Eq. (1) [44,45]. When a gel with small pore size (typically around ~5 nm) is dried slowly, clusters of partially dry regions are formed inside the gel body, as shown in Fig. 2, while the exterior surface remains wet [44]. The dried regions, homogeneously formed throughout the gel body, most likely suppress the spatial gradient of the stress that leads to fracture. A theory of the drying mode has been developed, indicating that this cavitation is possible only if the pore entry is small enough to induce capillary tension exceeding a critical value for the nucleation of bubbles inside the gel [46]. Interestingly, at a fast drying rate, the same gel is dried in the conventional way, and the cavitation is largely suppressed. Thus, cavitation during drying may be another, largely overlooked benefit of slow drying (Table 1) to obtain monolithic dried gels. After complete drying, relatively transparent gels are obtained (Fig. 3) [9,44], and they can be sintered into monolithic glasses [9].

2.2. Macroporous gels through phase separation

The average pore sizes of gels derived from the conventional hydrolysis and polycondensation of silicon alkoxides are usually

Table 2
Gelation times and pH of TEOS solutions containing different catalysts.

Catalyst	Catalyst/TEOS molar ratio	Initial pH of solution	Gelation time (h)
HF	0.05	1.90	12
HCl	0.05	0.05 ^a	92
HNO ₃	0.05	0.05 ^a	100
H ₂ SO ₄	0.05	0.05 ^a	106
CH ₃ COOH	0.05	3.70	72
NH ₄ OH	0.05	9.95	107
No catalyst	–	5.00	1000

Source: Ref. [29].

^a Between 0.01 and 0.05.

Table 3

Properties of xerogels prepared from TEOS solutions containing different catalysts and dried at 25 °C or heat treated at 600 °C.

Catalyst	25 °C				600 °C				
	Volume shrinkage (%)	Bulk density (g cm ⁻³)	Apparent density (g cm ⁻³) ^a	Porosity ^b (%)	Volume shrinkage (%)	Bulk density (g cm ⁻³)	Apparent density ^a (g cm ⁻³)	Porosity ^b (%)	Vickers' hardness
CH ₃ COOH	84.0	1.32	1.33	0.7	–	2.08	2.12	1.9	666.5
HCl	81.3	–	–	–	85.2	2.06	2.12	2.8	429
HNO ₃	79.9	1.14	1.16	1.7	85.2	1.82	2.02	10.0	470
H ₂ SO ₄	71.6	–	–	–	80.0	1.46	2.12	31.0	224
HF	78.4	0.54	1.24	56.7	82.7	0.71	2.13	67.0	75
NH ₄ OH	67.8	0.49	1.13	57.0	71.7	0.70	2.21	68.0	28
No catalyst	87.5	0.95	2.09	54.6	–	1.25	2.21	43.4	–

Source: Ref. [29].

^a Density of the gel matrix.^b $[1 - (\text{bulk density})/(\text{apparent density})] \times 100$.**Fig. 2.** Photograph showing a close-up view of dry clusters (white regions) in a wet gel with an average pore size of ~2.2 nm.

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less than ~50 nm. However, they can be increased significantly by inducing the macroscopic phase separation of precursor solutions into silica-rich and solvent-rich phases in parallel with gelation. This technique is quite useful in obtaining monolithic macroporous gels from alkoxide-based solutions with short processing times. The basic concepts and examples of macroscopic phase separation in tetraalkoxysilane-based gelling systems have been reviewed [47]. The resultant gels exhibit macroporous morphologies characteristic of spinodal decomposition, ranging from cocontinuous (interconnected) to fragmented structures, depending on the volume fraction of the silica-rich phase and the reaction rates (e.g.,

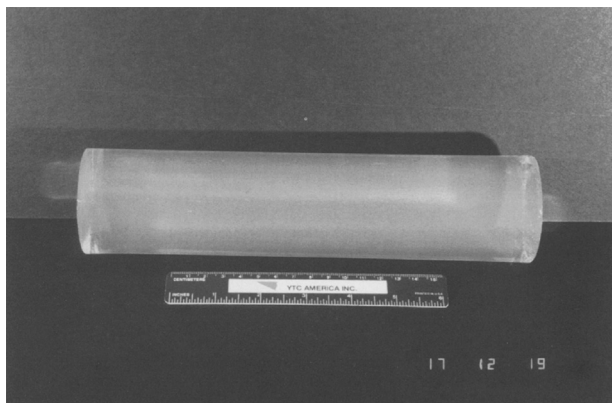
**Fig. 3.** Photograph of a monolithic alkoxide-derived dried gel, dried within 7 days. Reprinted with permission from Ref. [9]; Copyright 1996 Springer.

Fig. 4). The incorporation of organic polymers such as poly(ethylene oxide) and poly(acrylic acid) facilitates the control of the morphology; this technique has been utilized to form monolithic silica columns for high-performance liquid-phase chromatography (HPLC) [47,48].

In polymer-free tetraalkoxysilane-based systems, macroscopic phase separation is typically observed at low (≤ 2) water to alkoxide molar ratios in the presence of polar solvents such as formamide [47,49,50] (Fig. 4) and methanol [51]. In these cases, silica oligomers remain hydrophobic because of the lack of water to completely hydrolyze the alkoxy groups. As the polycondensation proceeds, the freedom of the chemical configurations of the silica oligomers decreases. Thus, the mixing entropy between the silica and solvent phases decreases, resulting in an exsolution of the silica oligomers from the hydrophilic solvent phase. Methanol is less polar than formamide. In a TMOS–water–methanol system, phase separation is observed only under highly acidic conditions; this may be due to an increase in the ionic strength of the solvent phase [51]. A similar mechanism may account for the formation of macroporous gels in a system consisting of TMOS, concentrated HCl, and ethylene glycol [52]. Because the macroscopic-scale silica domains scatter visible light significantly, the resultant gels are always opaque.

Although water is a highly polar liquid, little attention had been paid to macroscopic phase separation in additive-free tetraalkoxysilane-based systems at high (≥ 4) water to alkoxide molar ratios, at which most of the alkoxy groups can be hydrolyzed. However, in neutral pH ranges, hydrolysis is slow in contrast to the fast polycondensation (Fig. 5) [2,53], and hydrophobic silica oligomers modified with unhydrolyzed alkoxy groups may grow in a water-rich solvent. A similar idea has been employed using 2-propanol as a cosolvent to form highly porous xerogels modified with unhydrolyzed 2-propoxy groups [54]. The resultant gels exhibit cocontinuous morphology peculiar to macroscopic phase separation. The increase in the number of surface 2-propoxy groups is explained by a decrease in the hydrolysis rate as a result of the substitution of 2-propoxy for ethoxy groups [2], and an enhancement of the back reaction (esterification) under the alcohol-rich conditions. This technique to form macroporous gels has recently been utilized to fabricate monolithic silica glasses [55,56] (Fig. 6).

Macroscopic phase separation in a TEOS–water binary system under water-rich conditions has recently been realized by employing (i) two-step mixing that separates the partial hydrolysis and polycondensation stages and (ii) formation of a buffer system to stabilize the pH of the gelling solutions in the near-neutral pH range [57–59]. In the first step, TEOS is partially hydrolyzed with dilute nitric acid at a water to TEOS molar ratio (x_1) of ~2 (solution 1). Then, the solution pH is shifted to the neutral range by adding a solution of a weak base or a salt of a weak acid (solution 2). This procedure improves the reproducibility of the pH control, when

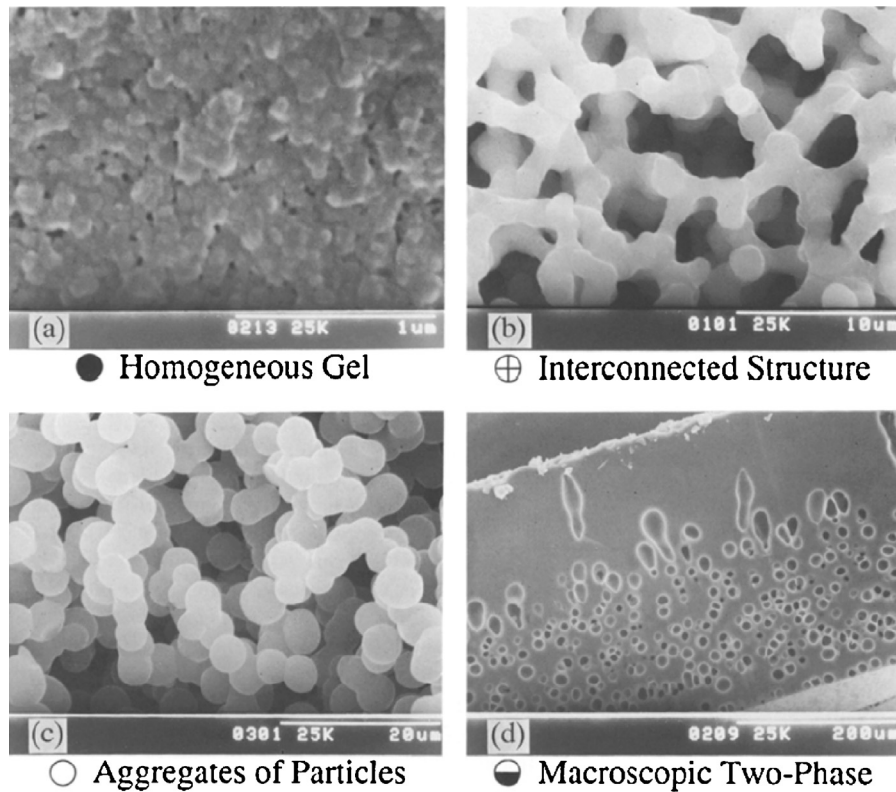


Fig. 4. SEM images of dried gels prepared from a tetramethoxysilane (TMOS)–water–formamide ternary system catalyzed by nitric acid. The TMOS:formamide:H₂O molar ratios and molar concentrations of nitric acid are (a) 1:2.5:1.6 and 1.0 M, (b) 1:2.5:1.5 and 0.6 M, (c) 1:2.5:1.5 and 1.4 M, and (d) 1:2.5:1.4 and 1.0 M, respectively. Reprinted with permission from Ref. [49]; Copyright 1993 Springer.

compared with simple neutralization using a strong base (e.g., NH₃). Table 4 lists typical solution compositions, and Fig. 7 shows the appearance and SEM images of the resultant dried gels prepared at $y = 0.01$ using ammonium acetate as a Brønsted base [58]. Fig. 8 shows the variation of the average pore size with the amount (y) and type of Brønsted base, demonstrating that the y value at which the pore size is maximized decreases by replacing the acetate salts (acetic acid: $pK_a \approx 4.8$) with more neutral bases such as imidazole ($pK_a \approx 7.0$) and ethylenediamine ($pK_{a1} \approx 9.9$, $pK_{a2} \approx 7.1$) [59]. The peak y value of the ethylenediamine system is about half of that of the imidazole system because ethylenediamine consumes two protons per molecule. It is noteworthy that the appearance and macroscopic morphology vary significantly, even if the final solution composition is unchanged while maintaining constant $x_1 + x_2$. As x_1 decreases, the fraction of unhydrolyzed ethoxy groups increases, the macroscopic phase separation is enhanced, and the fracture becomes less prominent. Because of the macroporous morphology, drying is relatively easy and the resultant gels are readily converted into silica glasses by sintering in a helium atmosphere at 1200–1300 °C without cracking (Fig. 1) [57,59].

Table 4

Typical molar ratio of constituents used to form monolithic macroporous silica gels from a TEOS–water binary system containing small amounts of pH control agents. Addition of solution 2 into solution 1, which is prehydrolyzed at $x_1 \lesssim 2$, causes macroscopic phase separation in parallel with gelation.

Solution 1			Solution 2	
TEOS	H ₂ O	HNO ₃	H ₂ O	Base
1	x_1	0.002	x_2	y

Source: Refs. [58,59].

Because alkoxides are hydrophobic and incompatible with water unless hydrolyzed, alcohols are frequently used as cosolvents to effect homogeneous mixing. However, the alcohols are removed during drying, and are not essential to the formation of monolithic gels [60] and glasses [61]. The recipe listed in Table 4 does not require the addition of alcohols. The use of pH control agents is also minimized. Furthermore, the gelation time is relatively short (~1 h) for acid-catalyzed TEOS-based systems, because the phase separation concentrates the silica oligomers and enhances their polycondensation. Thus, this procedure enables the fabrication of monolithic silica gels and glasses in a relatively short time while reducing the use of reagents.

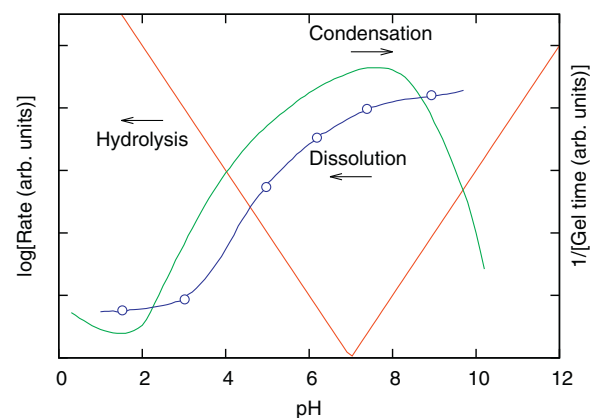


Fig. 5. Schematic representation of the pH dependences of the hydrolysis, polycondensation, and dissolution rates. After Refs. [2,53].

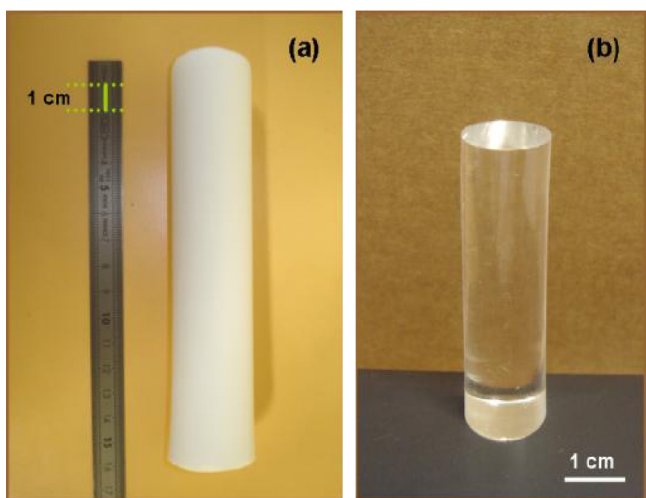


Fig. 6. Photograph of a sol-gel-derived silica gel stabilized at 1000 °C (a) and a silica glass rod prepared from the gel after dehydration and densification (b).

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3. Doping with metallic or nonhalogen elements and their compounds

3.1. Binary and multicomponent glasses

Sol-gel method is a melt-free process and is advantageous for preparing glasses with high melting temperatures, high crystallization tendencies, and compositions within the stable or metastable liquid-liquid immiscibility region. Thus, it has been used to form various monolithic binary silicates containing B_2O_3 [62–64], Al_2O_3 [62,65], TiO_2 [66–71], ZrO_2 [72], GeO_2 [16,40,73–75], Bi_2O_3 [76], and alkali [77,78] and alkaline earth oxides [79,80]. Multi-component glasses have also been fabricated [3,4,81–84]. Binary titanosilicate glasses containing ~5–10 wt.% TiO_2 are difficult to form by conventional processes and are applicable to low thermal expansion glasses [70,71]. Silica glasses doped with Bi ions have recently been prepared [76], because the broad infrared (IR) photoluminescence (PL) near the optical telecommunication wavelength region (~1.5 μm) is attractive for broadband optical amplification.

Spatial distribution of specific cations in monolithic gels can be modified by leaching or ion exchange, and these techniques have been utilized to form gradient-index (GRIN) lenses [85–89]. The mechanical strength of silica glasses is improved by incorporating nitrogen atoms, because they enter into the glass network with threefold coordination and increase the bond density.

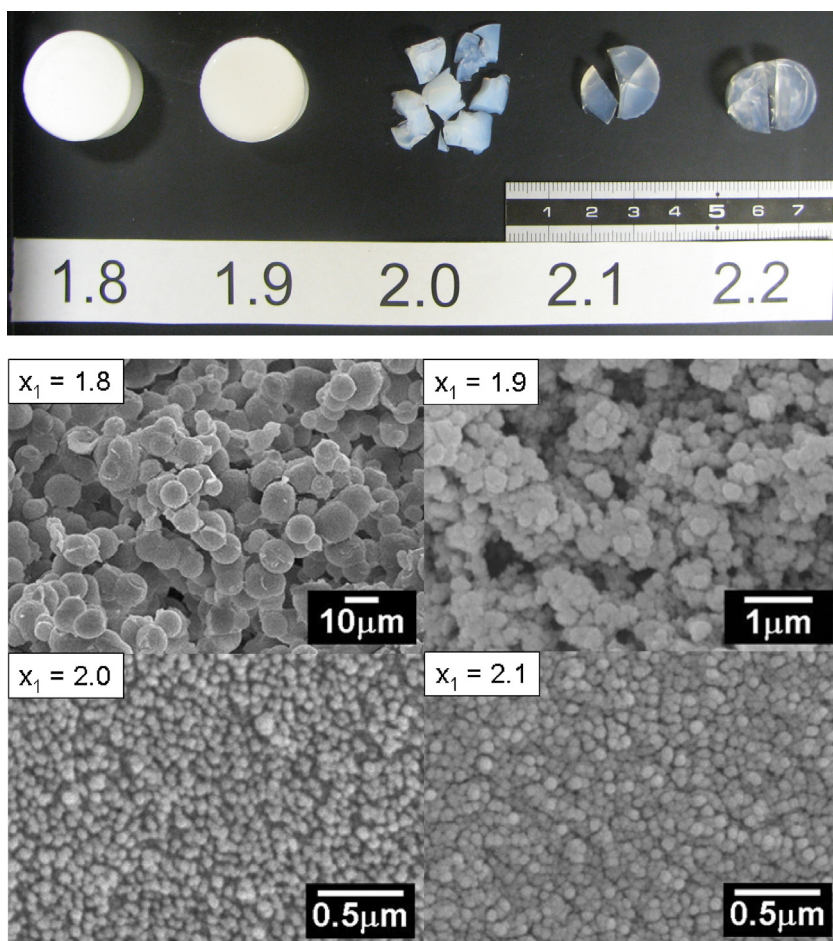


Fig. 7. Photograph (top) and SEM images (bottom) of dried gels derived from the composition listed in Table 4 at $x_1 + x_2 = 10$, $y = 0.01$, and 20 °C using 25 mmol of TEOS. Ammonium acetate is used as the Brønsted base. The x_1 value of each gel is shown in the pictures.

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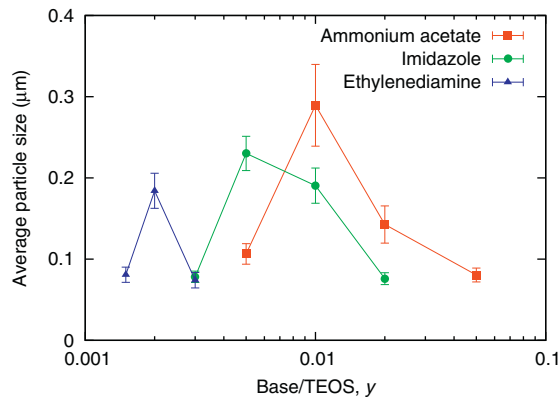


Fig. 8. Compositional dependence of the average particle size of gels prepared using different Brønsted bases, at the composition listed in Table 4 at $x_1 = 1.9$ and $x_1 + x_2 = 10$. After Ref. [59].

Monolithic oxynitride glasses have been prepared by sintering multicomponent silicate gels in flowing NH_3 [90].

3.2. Rare-earth doping

Rare-earth (RE)-doped silica glasses are important as phosphors, scintillators, and active gain media of solid-state lasers [91–93] because of their excellent transparency over a wide spectral region, good chemical and mechanical properties, high radiation hardness, and compatibility with preexisting silica-based fiber devices. Presently, most of RE-doped silica glasses for optical applications are prepared by vapor-phase methods such as vapor-phase axial deposition (VAD) and chemical vapor deposition (CVD), which are capable of rapidly synthesizing large high-purity monoliths. However, the low vapor pressure of RE compounds makes the direct vapor-phase loading of RE ions difficult, and immersion of a soot in a solution of dopant salts is usually not suitable for homogeneous doping with RE ions at high concentrations.

An advantage of the sol–gel method is that doping at high concentrations is easier than the conventional vapor phase methods. Monolithic silica glasses with RE_2O_3 concentrations larger than 1×10^4 ppmw (1 wt.%) can be obtained relatively easily [61,94–104]. Although samples sintered below 1000°C are often not densified completely and remain porous [95,99,105], the sintering temperature may be lowered for acid-catalyzed, less porous gels [94,101]. The upper limit of the RE_2O_3 concentration at which to obtain clear, fully densified glasses is most likely at ~ 5 – 10 wt.% [95,96,98–100]. Above such concentrations, the aggregation of RE ions and the devitrification become significant because of the low equilibrium solubility of RE ions in silica glass [106].

A good dispersion of RE ions in a host material is necessary to increase the PL efficiency while suppressing concentration quenching. Aluminum (Al) has been used most frequently to promote the dissolution of RE ions in silica glasses [107–125], including sol–gel-derived ones [110–113,115–117,119,121,122]. The formation of double metal alkoxides of RE and Al seems promising to further improve the dispersion of RE ions in silica glasses [111]. The effect of Al codoping on the coordination around the RE ions in sol–gel-derived silica glasses has been examined using optical absorption [112], PL spectroscopy [113,115,122], and molecular dynamics simulations [122]. The Al codoping increases the barrier height of the persistent spectral holes in sol–gel-derived glasses doped with Eu^{3+} ions [126]. The PL efficiency of RE ions in sol–gel-derived glasses is often lowered by the relatively high



Fig. 9. Photograph of a He–Ne interference pattern through a Nd–Al codoped silica glass (Nd_2O_3 , 1.25 wt.%; Al_2O_3 , 2.72 wt.%), sized $93 \text{ mm} \times 28 \text{ mm} \times 11 \text{ mm}$, prepared by sintering aluminosilicate zeolite powders loaded with Nd^{3+} ions. The optical quality is sufficiently good for the amplification experiment.

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SiOH concentrations, and its improvement by dehydration has been performed in an Er–Al codoped system [117]. Aluminosilicate zeolites loaded with RE ions are useful both as fillers and Al sources in the formation of monolithic silica gels and glasses containing both RE and Al ions. Because of the relatively high sintering temperature ($\geq 1750^\circ\text{C}$), the concentration of SiOH groups is effectively lowered. Large monolithic Nd–Al codoped silica glasses, as typically shown in Fig. 9, have been fabricated using Nd-loaded zeolite X powders [36,127]. The resultant glasses have high thermal shock parameters, and their applications as a 40J class high power laser [128] and a short (5 cm) fiber laser [129] have been demonstrated.

Another promising additive is phosphorus (P) [108,130–132]. Selective coordination of RE ions by phosphorus has been confirmed by pulsed electron paramagnetic resonance (EPR) [123,133]. However, phosphorus codoping has attracted much less attention than aluminum codoping. Persistent spectral hole burning in Eu–P codoped glasses [126], and the structure and PL properties of monolithic Ce–P and Ce–P–B codoped silica glasses [134], have been examined. More recently, the preparation of clear monolithic RE–P codoped silica glasses from solutions containing fumed silica has been reported [135].

The cosolvent-free synthesis of macroporous silica gels from phase-separating solutions, described in Section 2.2, has been used to form RE-doped glasses. Monolithic glasses with good transparency have been obtained by incorporating P or Al as codopants, as shown in Fig. 10 [136,137]. Despite the high SiOH concentration ($\sim 10^{20} \text{ cm}^{-3}$), the Tb–P codoped glasses exhibit bright green PL under ultraviolet (UV) photoexcitation, as shown in Fig. 11 [136]. The PL decay kinetics is a single exponential, and the PL intensity increases proportionally with Tb to Si molar ratios up to 0.02 ($\sim 5 \times 10^4$ ppmw or ~ 5 wt.% Tb_2O_3), while maintaining the PL decay constant at ~ 4.0 ms. The effect of Al codoping on IR PL properties has been examined in Nd–Al codoped glasses [137].

3.3. Incorporation of nanoparticles

Glasses containing nanoparticles can be transparent when the size of the nanoparticles is sufficiently smaller than the wavelength of light. Various monolithic transparent fully densified glasses containing nanoparticles have been prepared by the sol–gel method. In several binary silicates, including SiO_2 – RE_2O_3 systems, thermal annealing often causes precipitation of the second component-rich phases [110,121]. In SiO_2 – RE_2O_3 systems, the RE-rich phases are often not crystallized [138,139]. This phenomenon has been

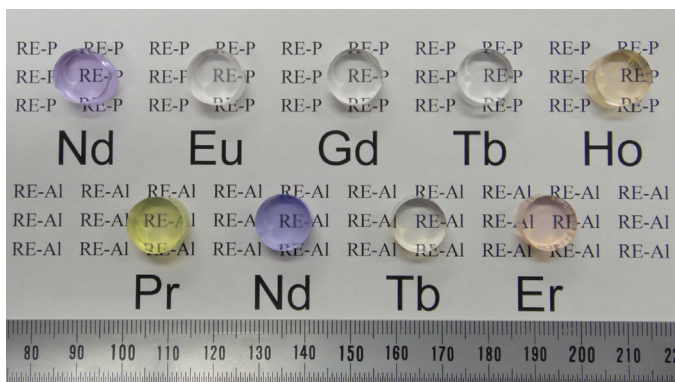


Fig. 10. Photograph of various RE–P and RE–Al codoped silica glasses prepared at RE to Si and P/Al to RE molar ratios of 0.01 and 1, respectively, in the precursor solutions. After Refs. [136,137].

utilized to form Fe_2O_3 [140], CeO_2 [141], Er_2O_3 [142], and Cr_2O_3 [143] nanoparticles, and their optical and magnetic properties have been examined. The formation of CeO_2 nanoparticles has been investigated along with the scintillation properties of coexistent Ce^{3+} ions [141,144]. The formation of SnO_2 nanoparticles in SiO_2 – SnO_2 binary systems has been well examined [145–148]. The use of less reactive tin precursors such as dibutyltin diacetate facilitates the incorporation of SnO_2 nanoparticles while suppressing their excessive growth (Fig. 12) [145]. However, a more recent study has shown that SnCl_2 , a more general tin source, is also usable for the preparation of glasses containing SnO_2 nanoparticles at high concentrations [148]. The SnO_2 nanoparticles can be used both as a low phonon energy host and a sensitizer of RE ions. It has been reported that the PL intensities of Eu^{3+} [149,150] and Er^{3+} [151,152] ions in silica glasses are enhanced by the precipitation of SnO_2 nanoparticles. Silica glasses containing $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$, which is attractive as an inorganic scintillator crystal, have been prepared by the crystallization of SiO_2 – Lu_2O_3 binary glasses [153,154].

Glasses doped with metal and non-oxide nanoparticles exhibit large optical nonlinearities, and they are often difficult to form by conventional melt-quench methods. Silica glasses containing CuCl [155], CuS [156], CuSe [157], and Au [158,159] nanoparticles have been prepared. Photonic crystal fibers have been drawn from preforms containing Au nanoparticles, and their nonlinear



Fig. 11. Green PL emission from Tb^{3+} ions in Tb–P codoped samples (Tb to Si molar ratios ranging from 0.001 to 0.02 at a P to Tb molar ratio of 1) exposed to UV light (254 nm) from a mercury lamp.

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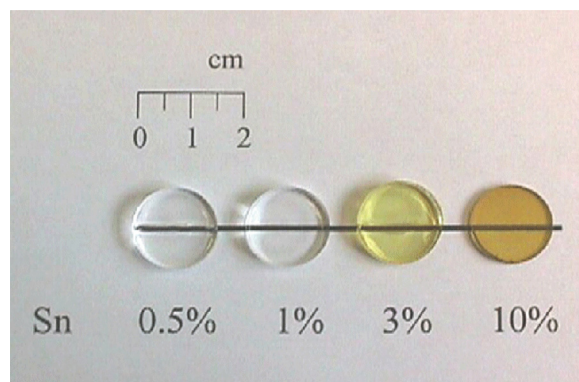


Fig. 12. Photograph of monolithic tin-doped silica glasses. The tin content (mol%) is indicated.

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optical properties have been examined [159]. Another interesting technique for the formation of nanoparticles is via reduction with H_2 , because H_2 diffuses rapidly in silica glasses at high temperatures [160–162] and is mobile even at or below room temperature [162–165]. Thermal reduction in an H_2 atmosphere has been used to form Ge nanoparticles in SiO_2 – GeO_2 binary glasses [166]. High-pressure H_2 loading below 100°C followed by thermal annealing in air enables the homogeneous precipitation of Ag and Cu nanoparticles in sol-gel-derived silica rods (Fig. 13) [167]. Silica glasses containing fluoride nanoparticles will be described separately in Section 4.3.

Because the sintering temperature of silica glasses is relatively high ($\geq 1000^\circ\text{C}$), the growth of nanoparticles and their reactions with the host glass often become prominent, leading to a deterioration of the transparency. This problem can be avoided by employing host glasses with low-melting temperatures. Multicomponent silicate glasses containing various functional nanoparticles, including CdS [168], $\text{Bi}_x\text{Y}_{3-x}\text{Fe}_5\text{O}_{12}$ (BiYIG) [169], SbSI [154,170], and CdTe [154], have been prepared.

4. Fluorine doping

4.1. Properties of HF-catalyzed gels

Hydrogen fluoride (HF), which is usually handled in an aqueous form (hydrofluoric acid), is important both as an acid catalyst and a fluorine source in the sol-gel processing of silica gels. The effects of HF in hydrolysis and polycondensation have been well examined [2,29]. Table 2 shows the effects of different catalysts in solutions with TEOS:EtOH: H_2O :catalyst molar ratios of 1:4:4:0.05 on the pH and gelation time [29]. Although the HF-catalyzed solution is less acidic than the solutions catalyzed by strong acids (HCl, HNO_3 , and H_2SO_4), the gelation time is much shorter than those of the other solutions. In addition, the bulk density and porosity of the HF-catalyzed gel are similar to those of the base (NH_4OH)-catalyzed gel, as listed in Table 3. These observations suggest that the enhancement of the gelation is due to the participation of F^- ions, whose size and electronic structure are similar to those of OH^- ions. Similar to an OH^- ion, a F^- ion acts as a nucleophile and reacts with an Si atom to form an Si–F bond [2,29,171]. The presence of Si–F bonds in dried gels has been confirmed by Raman [172] and IR [173] spectroscopies, through detection of the characteristic stretching mode [174,175]. A quantitative analysis using the lanthanum-alizarin complexone method indicates that nearly all the fluorine atoms are bound to

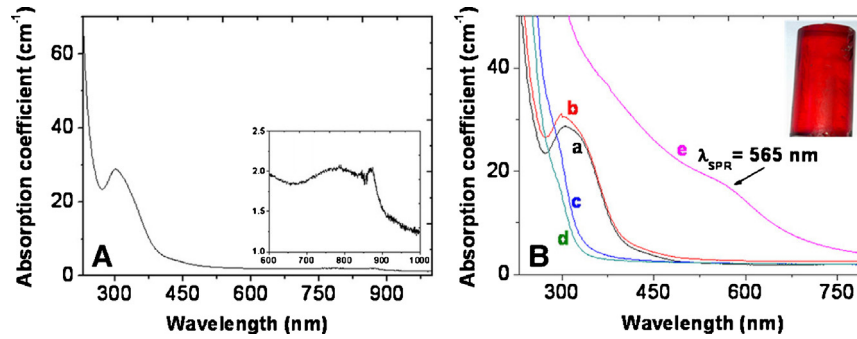


Fig. 13. Optical absorption spectra of silica glass doped with a copper precursor. (A) Before any reduction process; inset: scale expansion near 800 nm. (B) After hydrogenation at 80 °C without any further heat treatment (curve a) and after annealing at 100 °C (curve b), 300 °C (curve c), 500 °C (curve d), and 700 °C (curve e). Inset: a picture of the silica rod heated at 700 °C.

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Table 5
Effects of acid catalysts.

Catalyst	Wet gel ^a					Xerogel			
	Solution pH	Gelation time (days)	Aging shrinkage (%)	Rupture modulus (MPa)	Shear modulus (MPa)	Drying shrinkage (%)	Average pore diam. (Å)	Total pore volume (cm ³ g ⁻¹)	Surface area (m ² g ⁻¹)
HCl	0.6	3	10	0.46	1.72	38	22	0.49	920
HNO ₃	1.1	2.5	11	0.50	1.62	41	20	0.43	840
H ₂ SO ₄	1.1	2	11	0.50	1.89	40	22	0.41	790
Oxalic acid	2.1	2.5	9	0.31	1.26	45	20	0.44	850
HF	3.8	0.13	3	0.11	0.63	25	172	2.40	670

Source: Ref. [9].

^a Prepared at TEOS:EtOH:H₂O:catalyst molar ratio of 1:3:4:0.02 and aged for 7 days at 70 °C.

the silica phase of the HF-catalyzed gels prepared from a solution with a TEOS:EtOH:H₂O:HF molar ratio of 1:4:5:0.1 [176].

Table 5 summarizes several properties of gels prepared from solutions with a TEOS:EtOH:H₂O:catalyst molar ratio of 1:3:4:0.02 [9]. In addition to the relatively low acidity and short gelation time, large average pore diameter and pore volume are notable in the HF-catalyzed gel. Such large pore sizes and volumes are common in HF-catalyzed gels [9,176–178]. Thus, drying without fracture is easier for silica gels catalyzed by HF than for those catalyzed by conventional acids. In addition, the concentration of SiOH groups and the surface adsorption of H₂O are significantly suppressed (Fig. 14), suggesting that the surfaces of the gels are most likely covered by hydrophobic SiF groups [176,179,180]. This surface modification probably increases the contact angle θ with a hydrophilic solvent mixture and decreases the capillary pressure [Eq. (1)], additionally facilitating drying without fracture. These properties of HF-catalyzed silica gels are useful in the sol-gel synthesis of monolithic dried gels.

4.2. Fluorine doping and dehydration

Water is essential for the hydrolysis of alkoxides, and sol-gel-derived silica glasses usually contain a large number of SiOH groups, typically as many as $\sim 10^{20}$ cm⁻³ (~ 0.1 wt.%). Because SiOH groups terminate the Si–O–Si network and enhance structural relaxation [181,182], the presence of SiOH groups at moderate concentrations ($\sim 10^{17}$ to 10^{18} cm⁻³) is effective in improving the radiation hardness of silica glasses while eliminating heavily distorted sites that act as defect precursors. On the other hand, the O–H bond of an SiOH group is easily dissociated by radiation to form color centers ($\equiv\text{SiO}^{\bullet}$, a non-bridging oxygen hole center, NBOHC). Thus, the excess incorporation of SiOH groups is often detrimental to the radiation hardness [183,184]. In addition, SiOH groups significantly decrease the transmittance in the optical

telecommunication spectral range (wavelength at $\sim 1.5\mu\text{m}$). They also decrease the PL quantum yield of photoactive centers embedded in silica glasses.

The concentration of SiOH groups in silica glasses prepared from HF-catalyzed gels is much smaller than those in sol-gel-derived fluorine-free glasses. As described in Section 4.1, F⁻ ions added to precursor solutions react with silica oligomers to form SiF groups.

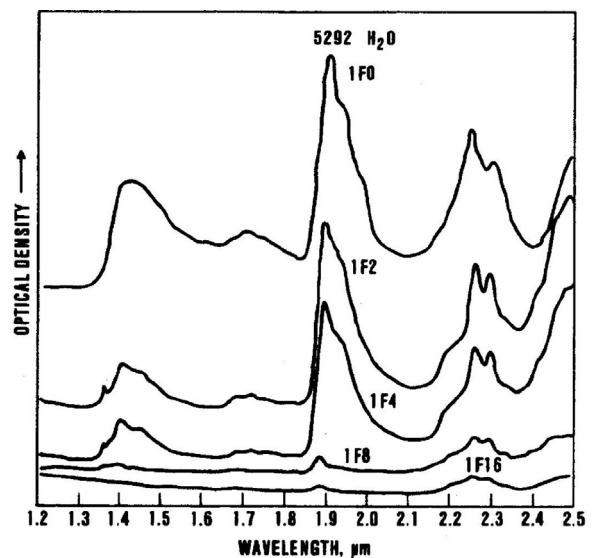


Fig. 14. IR absorption spectra of gels with fluorine contents ranging from 0 to 16 g per 100 g SiO₂ in the precursor solutions. The peak located at $\sim 1.9\mu\text{m}$ is attributed to H₂O molecules, and that observed at $\sim 1.4\mu\text{m}$ originates from both SiOH groups and H₂O molecules.

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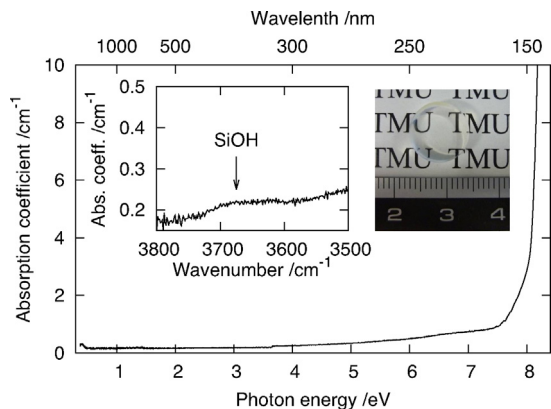


Fig. 15. Absorption spectrum and photograph of a fluorine-doped silica glass prepared from a solution with a TEOS:EtOH:H₂O:HF molar ratio of 1:4:5:0.1. After Ref. [176].

This surface modification diminishes the numbers of SiOH groups and adsorbed water molecules [176,179,180]. In addition, a portion of the fluorine is lost during sintering, mainly as HF and SiF₄ [179], and the fluorine loss is most likely accompanied by an additional loss of SiOH groups. An isolated SiF group is stable and hardly decomposes, even by heating at ~2000 °C [185]. However, a close pair of SiF and SiOH groups probably undergoes condensation to form HF as



The release of SiF₄ would be dominant only from gels with large F to Si molar ratios. Because SiF₄ is a dehydration agent, it would also participate in the removal of SiOH groups. In HF-catalyzed gels, the bloating at ~800–1000 °C because of the dehydration of neighboring SiOH pairs is suppressed [179], implying that most of the SiOH groups are removed below this temperature range. The concentration of SiOH groups in glasses derived from HF-catalyzed gels can be lowered to ~10¹⁷ cm⁻³ (~1 ppmw) by simply sintering them in helium [176] (Fig. 15).

Alkoxides containing SiF groups such as fluorotrimethoxysilane [173] and fluorotriethoxysilane [186–188] are also used to form fluorine-doped silica glasses with low SiOH concentrations. The properties of the resultant gels and glasses seem to be similar to those of samples derived from HF catalysis. A positive correlation is seen between the surface areas of the precursor dried gels and the maximum concentration of fluorine loaded in the resultant silica glasses [173].

The concentration of SiOH groups in sol-gel-derived silica glasses can be reduced by post-dehydration using halogen-based gases including Cl₂ [45,55,185,189,190], CCl₄ [191], SF₆ [192], and SiF₄ [185], or vacuum sintering [99]. These techniques are combined with liquid-phase fluorine doping to further reduce the concentration of SiOH groups [185,190]. The presence of fluorine in the dried gels is useful in reducing the use of the post-dehydration agents. Fluorine atoms in the form of SiF groups are not removed by dehydration with chlorine-based gases [185]. The concentration of SiOH groups in the resultant glasses can be much lower than 1 ppmw [189,191,190].

Apart from the reduction of the concentration of SiOH groups, SiF groups in silica glass have several useful properties. First, SiF groups do not exhibit optical absorption bands within the transparency window of silica glass [193–195]. Thus, dehydration by fluorine doping makes it possible to eliminate the optical absorption bands of SiOH groups at ~1.5 μm and ~170 nm, without introducing new absorption bands [176,186–188]. Second, SiF groups are stable and hardly participate in radiation-induced

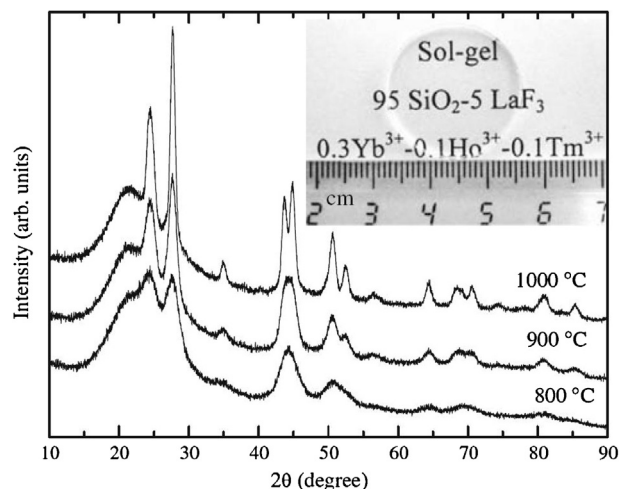


Fig. 16. XRD patterns of 95SiO₂-5LaF₃-0.3Yb³⁺-0.1Ho³⁺-0.1Tm³⁺ (at.%) glass-ceramics obtained by heat treatments at 800, 900, and 1000 °C. Inset shows a photograph of a transparent glass sample.

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defect processes [196,193–195,197]. In addition, similar to SiOH groups, they also enhance structural relaxation to remove heavily distorted defect precursor sites [198–201]. Thus, fluorine doping improves the radiation hardness of sol-gel-derived silica glasses [188]. Third, fluorine doping decreases the refractive index of silica glass [175,202–204]. This phenomenon is important in forming silica-based optical fibers and waveguides. Optical fibers with a triangular index profile have been prepared; the index profile was formed spontaneously, utilizing the evaporation of fluorine from the inner surface of a tubular gel during sintering [173].

4.3. Formation of monolithic silica glasses containing fluoride nanoparticles

Fluorides are attractive as host materials for luminescent centers because a relatively small phonon energy is suitable to suppress multiphonon relaxation. To overcome the relatively low chemical stability and mechanical strength of fluorides, glass-ceramics containing fluoride nanoparticles in oxide-based hosts, whose physical and chemical properties are better than fluorides, have been developed [205,206]. A major problem in the sol-gel processing of this type of glass-ceramic is that direct mixing between fluoride ions and metal cations in precursor solutions often results in the macroscopic precipitation of metal fluorides and loss of homogeneity.

A clever strategy to avoid these problems is to employ organic fluorine compounds as fluorine sources, because C–F bonds are stable in precursor solutions, but are decomposed during sintering to release fluorine atoms. Trifluoroacetic acid (CF₃COOH) has been used most frequently as the fluorine source. Through the pyrolysis of (CF₃COO)₃La, monolithic transparent silica-LaF₃ nanocomposites have been prepared [207]. This technique has been used to prepare monolithic silica glasses containing various types of fluorides, including REF₃ [208–211], and AREF₄ [212], where A denotes an alkali metal ion. Fig. 16 shows a photograph of a transparent silica glass containing LaF₃:Yb³⁺,Ho³⁺,Tm³⁺ nanoparticles and the X-ray diffraction (XRD) patterns [210]. These glasses are applicable to up-conversion devices [208,209,212] including white-light phosphors [210].

Despite the strong tendency for precipitate formation between fluoride and RE ions, monolithic transparent Nd-doped silica glasses have been prepared from a HF-catalyzed solution [99]. In

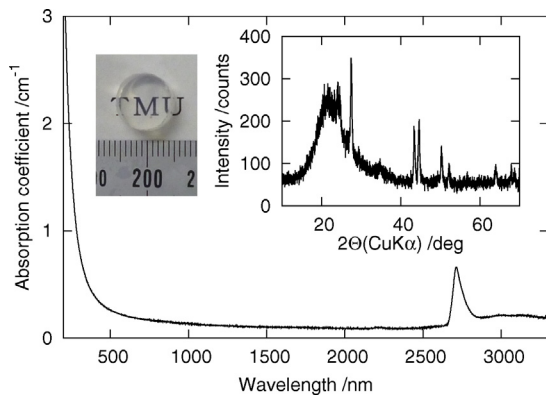


Fig. 17. Photograph, optical absorption spectrum, and powder XRD pattern of a silica glass containing LaF_3 nanoparticles, prepared from an HF-catalyzed TEOS-based solution with a TEOS:EtOH:H₂O:HF:HNO₃:La(NO₃)₃ molar ratio of 1:4:10:0.1:0.1:0.01. After Ref. [214].

this system, the concentration of SiOH groups is reduced significantly, while suppressing the precipitation of metal fluorides using methacrylic acid as a chelating agent. Fluorotriethoxysilane has also been used as a fluorine source to decrease the concentration of SiOH groups, and the formation of RE–F bonds has been confirmed in the resultant glasses [213]. Monolithic transparent silica glasses containing LaF_3 nanoparticles have also been recently prepared (Fig. 17) [214]. The macroscopic precipitation of LaF_3 is most likely suppressed by the absence of free F[−] ions in the precursor solution due to their trapping with silica oligomers in the form of SiF groups. Although the rapid growth of fluoride crystallites during sintering currently prevents an increase in the La to Si molar ratio beyond 0.01 while maintaining good transparency, the resultant gels have large pores that allow a reduction of the processing time.

5. Summary

Synthesis of monolithic silica gels and glasses is a basic research topic in the area of sol–gel processing. Although fracture during the drying of wet gels is still a major problem, it has largely been solved by supercritical drying and the addition of particulate silica fillers. On the other hand, the reduction of the surface tension of the pore liquid, controlled drying accompanied by the cavitation of the pore liquid, and macroscopic phase separation in parallel with gelation offer practical ways to reduce the fracture problem for gels that are prepared from alkoxides and dried under ambient pressure.

Other important issues in this field include further reductions of the processing time, the increase in the sizes of the product gels and glasses, the development of dehydration techniques, the reduced use of reagents, and the synthesis of functional glasses that are difficult to form by conventional melt–quench and vapor–phase methods. Macroscopic phase separation in alkoxide–water binary systems offers a unique opportunity to prepare monolithic silica gels without incorporating additives such as alcohols, organic solvents, and other reagents. Several promising routes toward the formation of monolithic functional silica glasses doped with rare-earth ions and/or nanoparticles while maintaining good optical transparency have been developed. Fluorination is particularly attractive for the functionalization of sol–gel-derived silica glasses because of its versatile effects such as increases in the pore size, the enhanced removal of SiOH groups, and the formation of photoactive nanoparticles of metal fluorides.

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