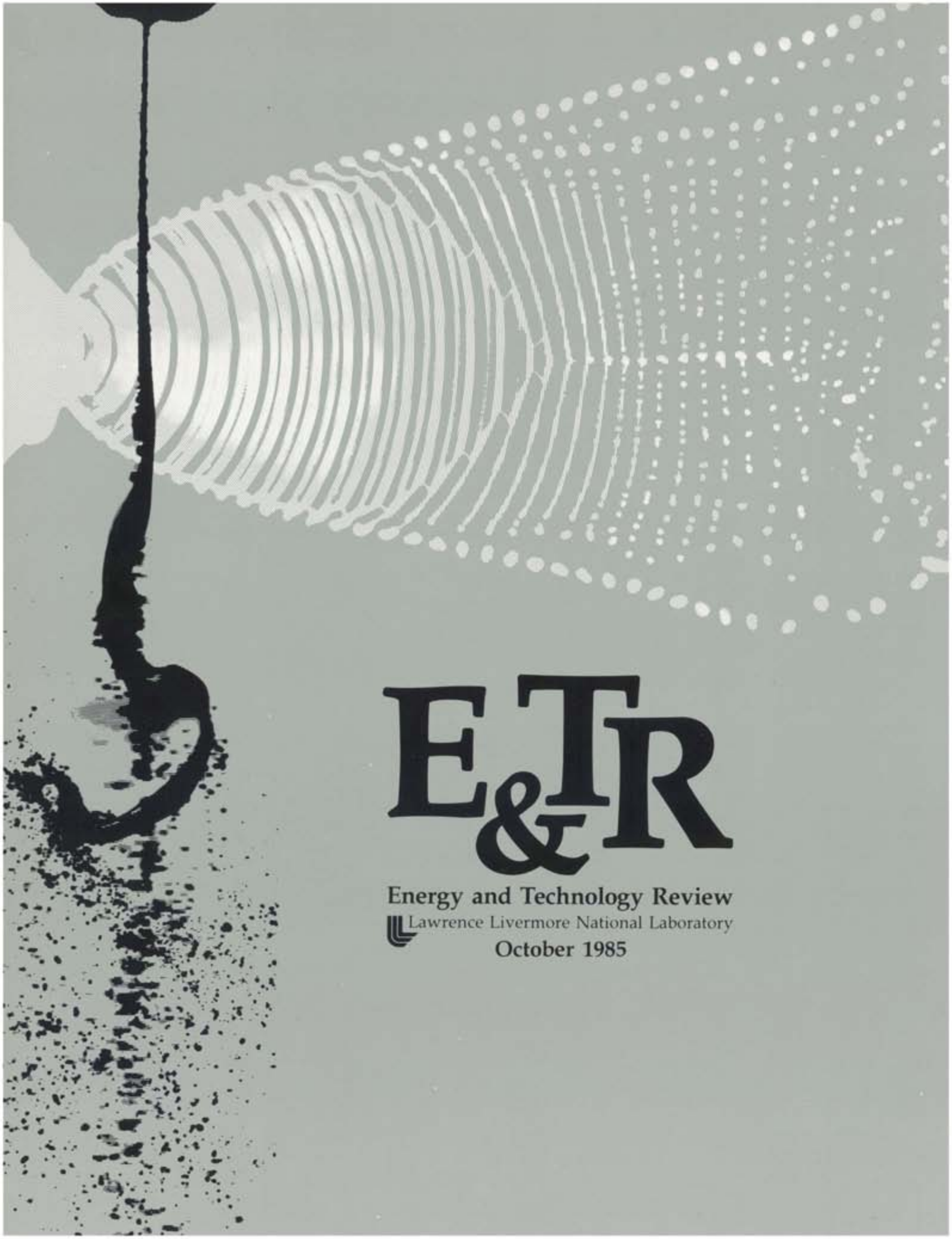

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Optical Coatings by the Sol-Gel Process

Our sol-gel process enables us to make highly damage-resistant, antireflective silica coatings for the large fused-silica lenses used in the Nova laser, and we are experimenting with a similar process to make damage-resistant dielectric mirrors.

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When light strikes a piece of polished glass, and again when it leaves, most of it is transmitted but some of it is reflected. The amount of reflected light and its degree of polarization depend on the angle of incidence. Even for normal incidence, however, the amount of reflected light can be as much as 5% per surface (both front and back).

For many purposes, this transmission loss can be tolerated; however, in a complex optical system containing many elements, the losses add up. To minimize these losses, it is common to apply some sort of antireflective coating. Many types of antireflective coating have been developed to improve the efficiency of optical systems. Most of these function by producing two reflections of equal intensity that cancel each other because one is 180° out of phase with the other.

When it comes to high-power optical systems such as the Nova laser, however, none of the common antireflective coating materials is suitable; they all suffer damage because particulate impurities cause spatially localized absorption of the intense laser light. One way to compensate for this might be to make the laser's optical elements of larger diameter, thereby reducing the light energy per unit area, but this would be far too expensive. Another way would be to limit the power of the laser, again reducing the energy per unit area, but this would limit the kinds of experiment that could be conducted. Instead, we elected to develop our own, highly damage-resistant, antireflective surface treatments that can withstand the power of the Nova laser.

One method that works well on lenses made of borosilicate glass involves etching the glass surface to produce a graded index of refraction.[1] It is the abrupt change from the index of refraction of air to that of glass that produces surface reflection. The porous surface layer provides a more gradual transition that eliminates most of the reflection.

Not all of Nova's optical elements could be made of borosilicate glass, however. Many of the experiments planned with the Nova laser require short-wavelength ultraviolet light, not the fundamental infrared wavelength. To convert the infrared light to shorter wavelengths, we pass it through an array of potassium dihydrogen phosphate (KDP) crystals. However,

upon exposure to ultraviolet light, borosilicate glass solarizes (turns brown and opaque). Therefore, for all optical components following the frequency-conversion array, we must use fused silica, the only material presently capable of transmitting high-intensity ultraviolet light.

Since fused silica has a different composition than borosilicate glass, etching it does not produce a porous layer. Hence, we had to develop another way to make a porous silica layer of controllable thickness. Silica, itself, is very damage resistant and thus would be an ideal material for an antireflection coating on fused silica.

The sol-gel process we have developed enables us to form, from solution, roughly spherical silica particles that are all approximately the same size. By varying the reaction conditions, we can vary the particle size from about 8 to 1000 nm; we have found that the best size for our antireflection coatings is 20 nm. Although the silica in these particles is dense, the spaces between the particles make a layer of them quite porous. The silica in the particles has an index of refraction of 1.46, but the overall index of refraction of the coating is about 1.22 because it is the average of the particles and the space between.

With the sol-gel process, we can also apply antireflection coatings directly to the KDP crystals, which would be damaged by exposure to the water or heat used in other coating processes. This greatly simplifies the construction of the frequency-conversion arrays, eliminating the need to sandwich the crystals between fused-silica windows and fill the assembly with index-matching fluid to eliminate internal reflections. With the antireflection coatings, the KDP crystals can be exposed directly to the laser beam.

The antireflection effect of such a layer is much greater at some wavelengths of light than at others, and the wavelength of maximum effect depends on the thickness of the coating. Fortunately, we can deposit additional layers to build up the coating to whatever thickness is required to match the desired optical wavelength.

The Sol-Gel Process

Our method for preparing damage-resistant antireflection silica coatings is a particular application of the sol-gel process,[2] a very versatile process for making metal oxides that involves:

- Dissolving one or more metal-organic compounds in an organic solvent.
- Gelling the resulting solution.
- Converting the gelled product, usually by drying and/or heat, to an oxide.

To make an oxide coating on a substrate using the sol-gel process, for example, we can spread the solution on the substrate and let the gelation take place passively by solvent evaporation. The form of the resulting oxide, whether dense or porous, depends on many factors, including the chemical makeup of the metal-organic compound used and the amount of water in the initial solution.

The general sol-gel process can be used with many different metals to form many different metal-organic compounds. To be suitable, the derivative compound should be readily convertible to the metal oxide or hydroxide, preferably by hydrolysis. An acceptable but less desirable alternative method of conversion is by thermal degradation.

Metal-organic compounds of the alkoxide class are particularly suitable for the sol-gel process. The generic chemical formula of the alkoxides is:

$$M(OC_nH_{2n+1})_x \quad ,$$

where M is a metal, n is an integer, x is the valence state of the metal, and the other symbols are the standard element abbreviations. Specific examples of the alkoxides of different metals include:

$$B(OC_4H_9)_3,\ Si(OC_2H_5)_4,\ Ta(OC_2H_5)_5 \ ,$$
$$Al(OC_4H_9)_3,\ Ti(OC_3H_7)_4,\ Nb(OCH_3)_5 \ .$$

All of these alkoxides are liquids, completely miscible with most organic solvents and readily hydrolyzed to give the metal oxide and the parent alcohol. The titanium alkoxide noted above, for example, combines with two molecules of water to form one molecule of titanium dioxide and four of propyl alcohol:

$$Ti(OC_3H_7)_4 + 2H_2O \rightarrow TiO_2 + 4C_3H_7OH \quad .$$

One way to deposit an oxide coating is simply to spread a solution containing one of these alkoxides uniformly on a substrate. Upon exposure to moist air, the solution will take up all the water needed for the hydrolysis reaction shown above. If we want to deposit a mixed-oxide coating, we can dissolve two or more alkoxides in the same solvent.

Another deposition method starts with the addition of a small quantity of water to the metal-organic solution to initiate hydrolysis. In many cases, particularly with silicon alkoxides, this leads to polymerization, and the product initially remains in solution. The solution at this stage can be applied to a substrate and converted to an oxide as before.

Alternatively, we can allow the polymerization to proceed to the gel stage; the solvent is retained but the metal derivative is now insoluble in the form of a crosslinked, three-dimensional structure. Subsequent treatment of this gel can produce porous or dense oxide products.

In some cases, the solution can assume yet another form: a discrete second phase consisting of extremely small, colloidal oxide particles instead of a gel. It is these colloidal solutions of oxide particles that we are using to make antireflective coatings for the fused silica and KDP optics in the Nova laser.

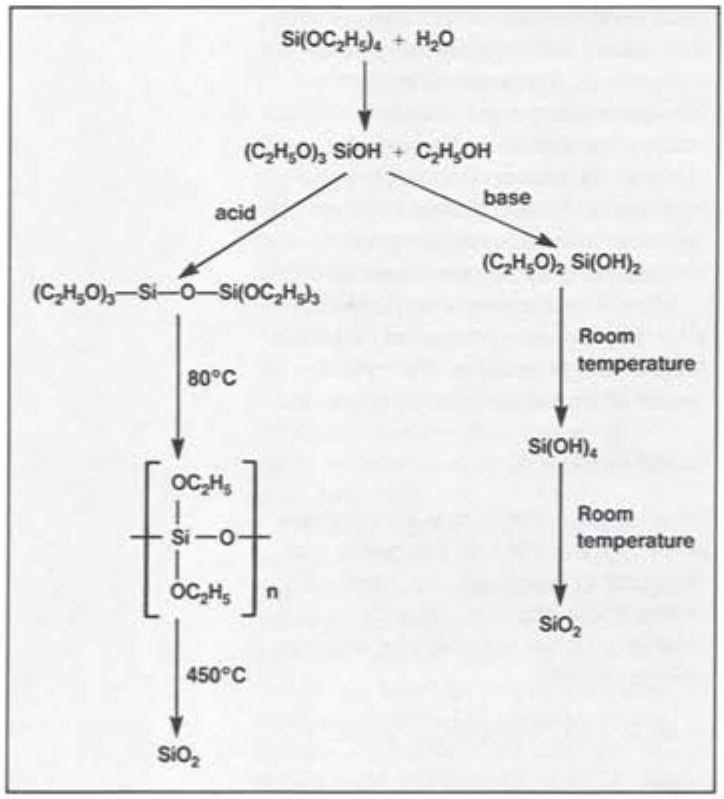


Fig. 1

Alternative reaction pathways in the hydrolysis of tetraethyl orthosilicate to silicon dioxide (silica). In the reaction using an acid catalyst, the coating consists of a polymer that degrades to silicon dioxide only at high temperature, sometimes leaving behind harmful organic residues. When the catalyst is a base, the reaction proceeds entirely at room temperature and yields pure silica.

Antireflective Coatings

Optical theory dictates that, for optimum performance, a single layer of antireflective coating for fused-silica optics have a refractive index of about 1.22. The refractive index of silica is about 1.46. Therefore, if we want to make the antireflective coating of silica, we will need to achieve a porosity of about 55%. The sol-gel process is particularly applicable under these conditions because it yields silica of the highest purity (required to keep the laser damage threshold high), and it is easy to obtain the required porosity.

In our investigation, our silica source is tetraethyl orthosilicate, $Si(OC_2H_5)_4$, a volatile liquid that boils at a temperature of 167°C and is readily purified by fractional distillation, thus giving very pure silica. Hydrolysis requires a catalyst that may be either acidic or basic. The pathway along which the reaction proceeds depends on the choice of catalyst, but the end product in either case is silica (see Fig. 1). The overall reaction is:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \quad .$$

At first, we investigated the acid-catalyzed system. The first step is to

dissolve the tetraethyl orthosilicate in boiling ethanol and partially hydrolyze it to produce a soluble ethoxysiloxane polymer. We applied this polymer to the substrate and converted it to silica by thermal decomposition (baking at 400°C), then further increased the porosity of the silica coating by etching it in a dilute solution of hydrofluoric acid.

Although the optical properties of the resulting coatings were quite satisfactory, some of the coatings failed under irradiation with laser light. The cause of these failures probably was incomplete thermal degradation of the organic components in the orginal siloxane. This would leave carbonaceous residues that would absorb energy, causing destructive hot spots in the coatings.

To avoid this source of trouble, we turned our attention to the base-catalyzed system, which produces a colloidal dispersion of silica particles in ethanol (Fig. 2). The preparation is carried out at room temperature and takes two to three days. The silica particles are roughly spherical and can be made in any diameter from about 8 to 1000 nm by varying the reaction conditions. After we prepared the base sol with silica particles of the preferred size (about 20 nm), the coating is applied simply by spreading the sol evenly on the substrate and allowing the ethanol to evaporate at room temperature. This eliminates high-temperature baking and with it the possibility of unwanted organic residues.

In Fig. 3, we compare transmission spectra of a 5-cm-diameter fused-silica disk at several stages in the process of coating it with three layers of the sol mixture. Two features of these spectra are immediately apparent: the narrow bandwidth over which transmission rises to almost 100% (that is, near-zero reflection), which is characteristic for this type of coating, and the shift in the specific wavelength for zero reflection as we apply additional coats of silica. This latter property makes it possible to tailor the coating for a desired wavelength range.

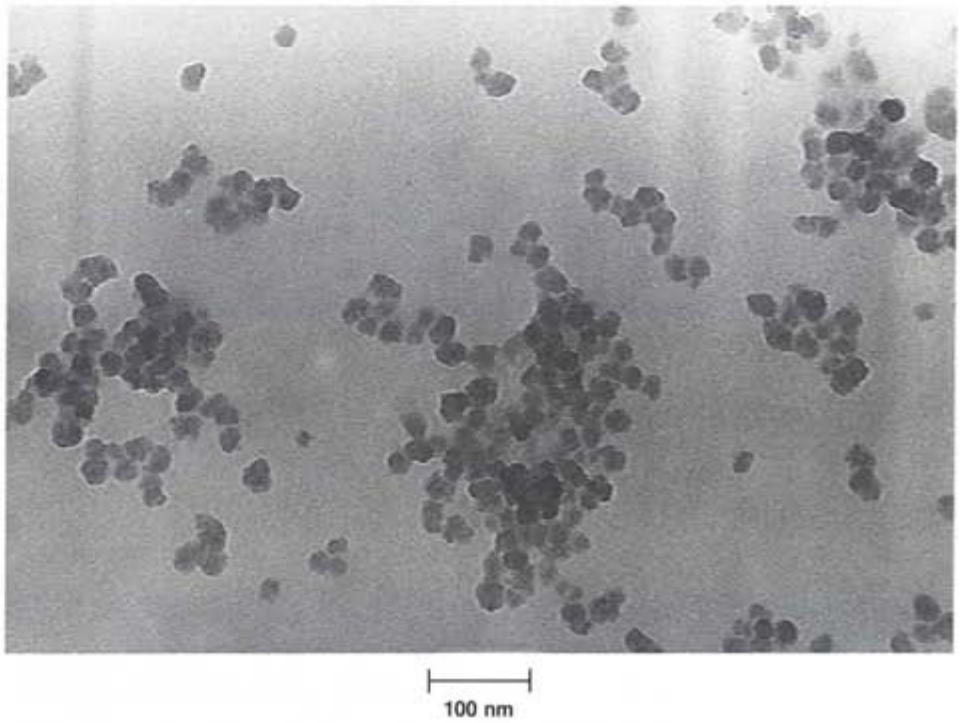


Fig. 2

Photomicrograph of the uniform colloidal particles of silica produced by the base-catalyzed sol-gel process. The particle size can be controlled by adjusting the reaction conditions. The refractive index of an antireflective coating made of these particles is less than that of the silica particles because it is averaged over the pores as well as the particles.

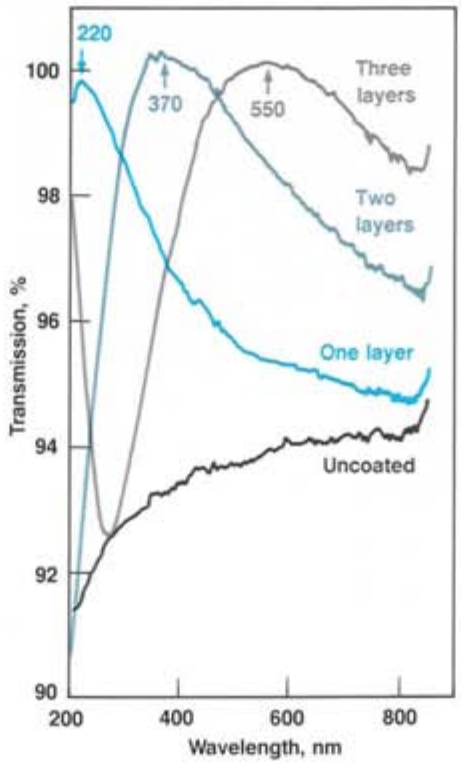


Fig. 3

Two-surface transmission spectra of a piece of fused silica illustrating the effect of adding successive layers of our antireflective silica coating. Uncoated, the fused silica reflects about 6% of the incident light over a broad range of frequencies (black). The first coating layer (blue) produces almost 100% transmission (zero reflection) but at a very short wavelength (220 nm). The second and third layers (blue-gray and gray) successively broaden the range of zero reflection and shift the peak to longer wavelengths.

Similarly in Fig. 4, we compare the transmission spectra of a 5- by 5-cm KDP crystal before and after receiving one coat of silica sol. Since the light changes to a shorter wavelength upon passing through the KDP crystal, the antireflection coatings must be of different thicknesses on the two sides, thicker on the first side that sees the infrared light and thinner on the second side that passes the converted, shorter-wavelength light.

Table 1 presents typical damage-threshold levels for coated fused-silica and KDP samples at various wavelengths, and compares them with the surface-damage thresholds of uncoated fused-silica samples and the bulk damage level of KDP. The coated fused-silica samples can withstand as much laser light as can uncoated fused silica; the sol-gel coatings outperform conventional antireflective coatings by three- to fivefold. Furthermore, the coating on the KDP crystal can withstand more intense laser irradiation than can the interior of many KDP crystals.

We have now thoroughly established this base-catalyzed sol process and have scaled it up from laboratory size to more than 750 litres, enough to coat the large Nova lenses. To obtain a uniform coating on these lenses, we set them on edge in a deep narrow tank filled with the coating sol and then drain out the sol at a constant rate (Fig. 5). Because this process produces coatings of equal thickness on the two sides, it is not suitable for coating the KDP crystal for the frequency-conversion array. Instead, we set the KDP crystal spinning on a turntable, and pour the coating sol gently in the center. Centrifugal force spreads out the liquid in a thin sheet, leaving a uniform coating on one side of the crystal. After enough layers have been applied to reach the desired thickness, we turn the crystal over and coat the other side.

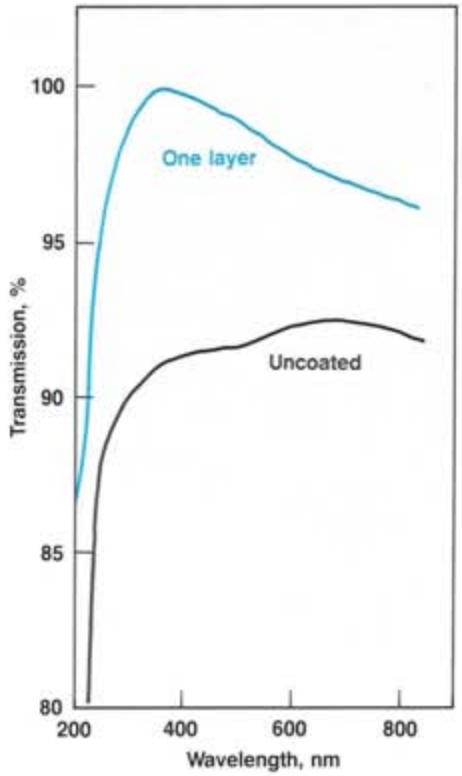


Fig. 4

Two-surface transmission spectra of a KDP crystal showing the effect of our antireflection coating. Uncoated, the crystal reflects 8 to 9% of the incident light over a broad range of frequencies (black). When coated with one antireflective layer (blue), the crystal transmits almost 100% (zero reflection) of the incident light for wavelengths near 380 nm.

Dielectric Mirror Coatings

Having learned how to manipulate the index of refraction of a surface coating to suppress reflections, we can turn the process around to produce highly reflective coatings to make the mirrors that turn and guide the laser beams. To do this, we coat the substrate with many alternating layers of a material with a high refractive index and one with a low index. As with the antireflection coating, the mirroring effect is specific for a particular wavelength range that depends on the thickness of the individual layers. Dielectric (nonmetallic) mirrors of this type are widely used in some laser applications but have been limited in other cases by their inability to withstand intense laser irradiation.

There are a number of oxides with high indices of refraction that are quite readily prepared from alkoxide starting materials by the sol-gel method. Among them are the oxides of titanium, zirconium, hafnium, tantalum, and niobium. The intervening layers of low-refractive-index material are commonly made of silica.

The dielectric mirror effect depends partly on the number of layers and partly on the difference between the indices of refraction of the two

materials. To minimize the number of layers and the expense and technical difficulty of fabrication, the difference must be as great as possible. Hence, the high-index layers should be as dense as possible so that they have the highest possible refractive index; this normally requires a high-temperature bake. The silica layers, because they should have the lowest practical refractive index, can remain porous.

We have been experimenting, so far, with dielectric mirrors produced only on a small scale, mostly with layers of tantalum oxide and silica. For the tantalum oxide layers, we have used two alkoxide starting materials: tantalum pentaethoxide, $Ta(OC_2H_5)_5$, and tantalum sesquichloride ethoxide, $Ta(OC_2H_5)_{2.5}Cl_{2.5}$. Either of these materials is applied to a substrate (usually fused silica) from solution and allowed to hydrolyze to form the oxide, as described earlier. The reactions are, respectively,

$$2Ta(OC_2H_5)_5 + 5H_2O \rightarrow Ta_2O_5 + 10C_2H_5OH \quad ,$$

and

$$2Ta(OC_2H_5)_{2.5}Cl_{2.5} + 5H_2O \rightarrow Ta_2O_5 + 5C_2H_5OH + 5HCl \quad .$$

We found that we could obtain coatings of high density with refractive indices of about 2.1 by baking the specimens at 150°C.

To make the silica layers, we use an acid-hydrolyzed ethyl silicate solution instead of the base-hydrolyzed system used for the antireflection coatings. We apply this solution to the substrate and heat it to 150°C as with the tantalum oxide layers.

On fused-silica substrates, we have been able to make durable dielectric mirrors thirteen layers thick, six layers of silica alternating with seven layers of tantalum oxide. Currently, mirrors with more layers tend to crack and peel during the baking operation, possibly because of stresses generated by differential thermal expansion.

Figure 6 shows the transmission curve of a nine-layer dielectric mirror (four layers of silica alternating with

Table 1 Typical damage threshold levels for silica antireflection coatings and optical materials used in the Nova laser.

Laser		Surface damage threshold		
Wavelength, nm	Pulse length, ns	Silica coating on fused silica, J/cm²	Bare fused silica, J/cm²	Silica coating on KDP, J/cm²
248	15	4–5	6–8	—[a]
353	0.6	8.5–10	10	>4–5[b]
1064	1.0	10–14	16	—

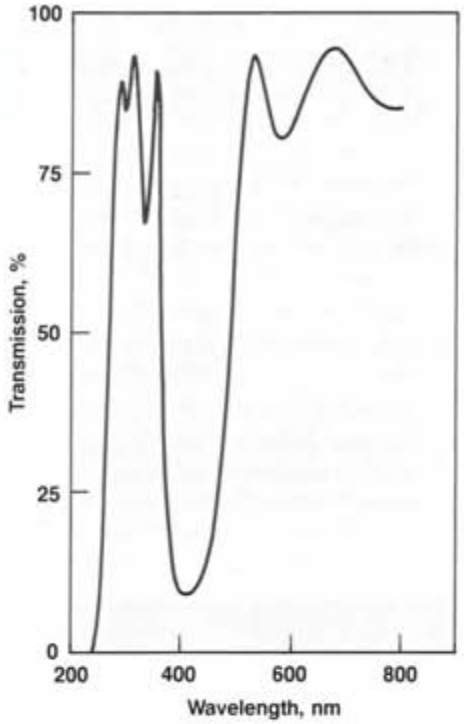
[a]Samples not tested at this wavelength.
[b]Damage threshold of the coating was not measured directly because bulk damage occurred first in those samples tested.

Fig. 5

One of the large (80-cm-diameter) fused-silica lenses for the Nova laser being lowered into the tank where it will receive its sol-gel antireflective coating. Once the lens is in place, the tank is filled with about 750 litres of colloidal silica solution. After a wait of about 15 minutes to allow the atmosphere between the liquid surface and the tank lid to come to equilibrium and all waves and ripples in the solution to dissipate, the liquid is drained away at a constant rate. The rate at which the liquid is drained away controls the thickness of the coating; a fast rate produces a thick coating, a slow rate a thin coating.

Fig. 6

Transmission spectrum of a dielectric mirror coating on one side of a fused-silica substrate. The coating consists of four layers of porous silica (low index of refraction) alternating with five layers of dense tantalum oxide (high refractive index). The deep dip at about 400 nm indicates that 91% of the light of this wavelength was reflected. Almost all the light of wavelengths longer than 500 nm was transmitted. The drop-off at wavelengths shorter than 270 nm is caused by absorption in the tantalum oxide layers.



five layers of tantalum oxide, all on a silica disk). This mirror reflects about 91% of the light at a wavelength of 400 nm. Longer wavelengths pass straight through with little loss; the tantalum oxide strongly absorbs wavelengths shorter than about 280 nm.

Summary

The sol-gel process is a versatile new method for preparing the oxides of many different metals and incorporating them in many types of coating. With this process, we have developed a superior method for preparing highly damage-resistant antireflection coatings of porous silica for the large fused-silica lenses and KDP frequency-conversion arrays used in the Nova laser. We also have produced small, experimental, damage-resistant dielectric mirrors of tantalum and silicon oxides with a variation of the sol-gel process. With this sol-gel method, we probably will be able to make damage-resistant antireflection coatings that can withstand lasers even more powerful than Nova. With further development, this sol-gel process can be extended to many other types of optical coating.

Key Words: alkoxide; coating—antireflection; damage threshold; frequency conversion; laser—Nova; lens—fused silica; light—ultraviolet; mirror—dielectric; potassium dihydrogen phosphate (KDP); sol-gel.

Notes and References

1. For a discussion of antireflective coatings for borosilicate glass optical components, see the March 1982 issue of *Energy and Technology Review* (UCRL-52000-82-3), p. 9.
2. The sol-gel process was described briefly in *Energy and Technology Review* (UCRL-52000-84-7), July 1984, p. 43.