Section 3
ADVANCED TECHNOLOGY DEVELOPMENTS

3.A Protective Polymeric Coatings for Nonlinear Optical Materials

Nonlinear optical materials (e.g., KDP and lithium niobate) have become important in high-power laser applications such as frequency conversion and laser Q-switching. The use of these materials, however, has been hampered by the unavailability of antireflective (AR) coatings with high laser-damage resistance and good mechanical and environmental durability. In this article, we shall describe one type of organosilicone resin that has been shown to be useful for the deposition of laser-damage-resistant AR and/or protective coatings on KDP, lithium niobate, and potassium pentaborate. We shall also describe the importance of these polysiloxane resins as an intermediate binding layer for the deposition of multilayer dielectric thin-film AR coatings onto KDP substrates.

The application of damage-resistant evaporated dielectric thin-film coatings onto KDP, KD*P, and lithium niobate has proven difficult. Dielectric thin-film coatings applied directly to KDP substrates are subject to fracture and poor adhesion due to the high coefficient of thermal expansion of KDP,[1] as compared to conventional optical materials such as fused silica and BK-7.[2] In addition, the hygroscopic KDP crystals can be readily damaged by the penetration of moisture through porous AR coatings or coating pinholes. As a result, index matching for KDP frequency-conversion cells has been accomplished by the use of such liquids as propylene carbonate or decalin.

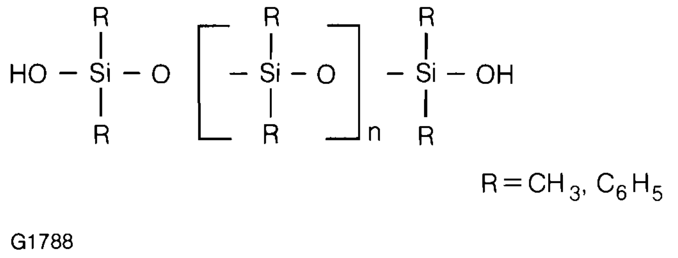
Resorting to an index-matching liquid to reduce Fresnel losses has resulted in complex fluid-filled cell geometries that are subject to leakage and thermal blooming from refractive-index changes of the fluid caused by localized heating. Recently, an antireflective coating for KDP that makes use of the sol-gel process to deposit a thin, porous layer of silica onto KDP substrates by spin deposition has been reported by Thomas *et al.* at Livermore.[3] Although this coating demonstrated high laser-damage resistance and good optical properties, its extremely poor adhesion allowed it to be readily removed by touching or wiping the coated surface. Additionally, the porous nature of the coating afforded no protection against moisture attack on the KDP substrate.

Potassium pentaborate and deuterated potassium pentaborate have been shown to be useful materials for second-harmonic generation and sum-frequency mixing for wavelengths shorter than 351 nm.[4] The presence of lattice water (or D_2O in the case of the deuterated material) is key in the origin of the nonlinear optical properties of these materials. Exposure of potassium pentaborate to the environment for prolonged periods of time results in loss of lattice water, with a subsequent loss in conversion efficiency and a substantial reduction of the optical quality of the crystals due to surface degradation. As with KDP, a protective coating with high laser-damage resistance and good optical quality would be most desirable.

A different situation holds for the deposition of AR coatings onto lithium niobate. A variety of dielectric thin-film materials that can be readily applied is available;[5] however, the unique physical properties of lithium niobate (ferroelectricity and piezoelectricity) result in temperature-induced surface charging of the material at the elevated temperatures required for evaporated thin-film deposition. This surface charging causes any particulate material present in the coating chamber to be attracted to the substrate and to become imbedded in the AR film during deposition, thus creating sites for laser damage.

Our interest in polysiloxane polymers as potential AR and protective coatings for nonlinear materials was initiated by recent reports[6] of the high laser-damage resistance of one commercially available class of resins manufactured by Owens-Illinois and known as "glass resins." These materials are prepolymerized, high molecular-weight polysiloxane resins that are terminated with silanol end groups and cured by condensation to yield rugged, insoluble coatings of high optical quality. The chemical structure of these polymers is shown in Fig. 27.5. Polysiloxane resins display high optical transmission in the near-IR to near-UV regions of the spectrum. The transmission characteristics of a cured 7-μm layer of a typical polysiloxane resin is shown in Figs. 27.6 and 27.7. The resin is essentially transparent in the 270-nm to 1800-nm region, with a slight improvement in transmission in the UV region after curing.

Earlier experiments performed at LLE[7] and elsewhere[8] have demonstrated the usefulness of polysiloxane resins in producing excellent quality homeotropic alignment in liquid-crystal devices for optical modulation and nonlinear optical applications. Table 27.V summarizes the physical properties of the polysiloxane resins that were used for coating



$$\mathrm{HO}-\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{Si}}}-\mathrm{O}\left[-\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{Si}}}-\mathrm{O}\right]_n-\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{Si}}}-\mathrm{OH}\qquad \mathrm{R}=\mathrm{CH_3},\ \mathrm{C_6H_5}$$

Fig. 27.5
Structure of polysiloxane "glass resin." The refractive index of the polymers is dependent on the organic side groups present (for methyl it is 1.42; methyl and phenyl, 1.43 to 1.55; phenyl, 1.56). The high laser-damage resistance of the polymers is believed to be due to additional purification steps taken during their synthesis.

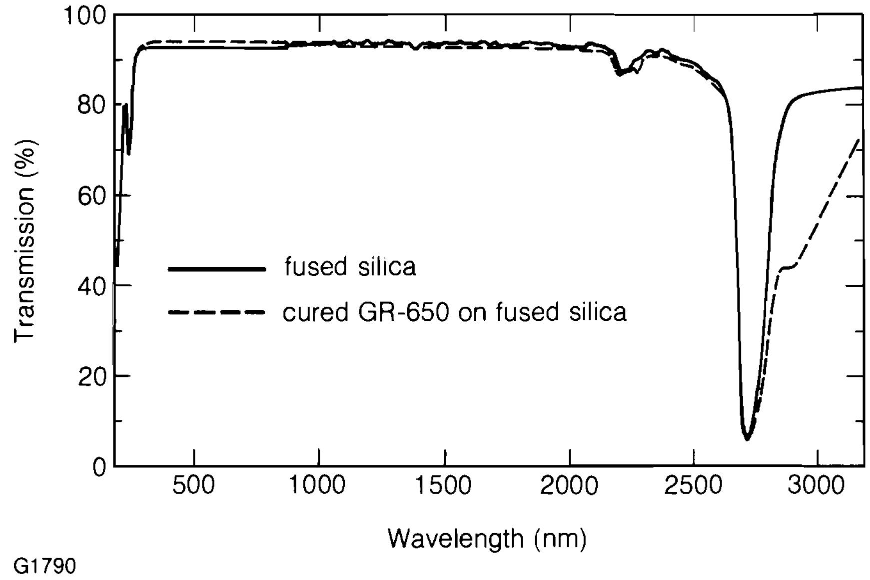


Fig. 27.6
Transmission spectra of fused silica coated on both sides with a 7-μm layer of GR-650 (total path length of polymer: 14 μm) and uncoated fused silica in the near-IR to near-UV region. Substrate thickness: 6.32 mm. The large peak at 2750 nm (fused silica) and the absorption edge at 2800–3000 nm (coating) are due to Si-OH bonds.

experiments with nonlinear optical materials. The availability of polysiloxane resins with refractive indices ranging from 1.42 to 1.56 (589 nm) affords the possibility of creating an index match between the coating and the substrate. This ability to index-match, coupled with the ability to produce particle-free, damage-resistant coatings of high optical quality with relatively simple equipment, made these materials ideal candidates for AR or protective coatings for problem materials such as KDP, lithium niobate, and potassium pentaborate.

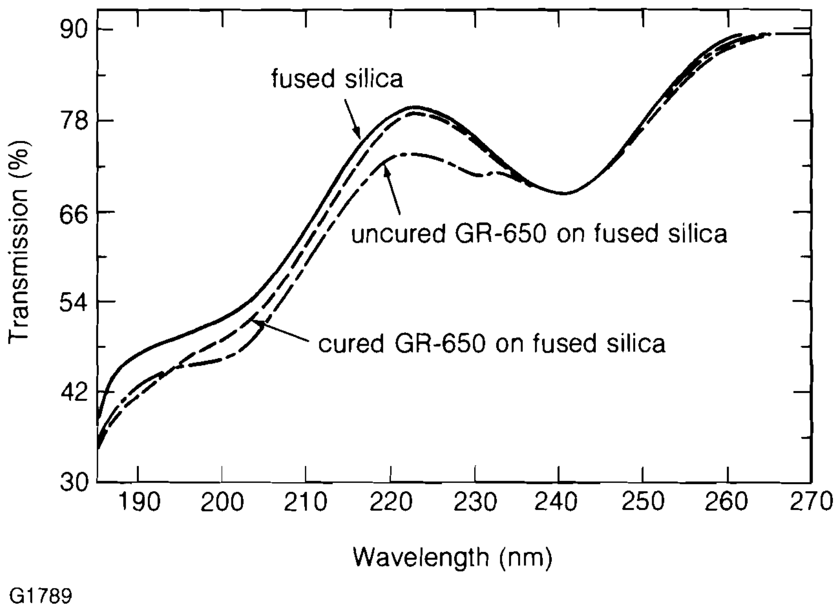


Fig. 27.7
UV transmission spectra of fused silica coated on both sides with a 7-μm layer of GR-650 (total path length of polymer: 14 μm) before and after coating at 120°C for 24 hours. Also displayed is the transmission of the fused silica substrate (6.32-mm thick) before coating. An increase in transmission of the coating in the UV region after curing is evident.

Table 27.V
Physical properties of Owens-Illinois polysiloxane resins.

Resin	Organic Side Group	% Solids Content	Refractive Index (589.6 nm)	Refractive Index (1064 nm)	Cure Temp/ Time
GR-650	methyl	100	1.42	1.4028	120°C/24 h
GR-651	methyl	27.5 (butanol)	1.42	---	120°C/0.5 h
GR-100	methyl-phenyl	100	1.49	---	120°C/24 h

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In the following sections, the coating experiments performed and the results obtained are described as they pertain to each of the nonlinear optical materials investigated.

Coatings for KDP and KD*P

1. KDP

Samples used for the KDP coating experiments were supplied by Inrad. The disk samples supplied were 50-mm diameter by 6.3-mm thick (scratch-dig 100/25), Type 2 cut, which had been polished by conventional means. All cleaning and coating operations were performed under Class 100 clean-room conditions in a horizontal laminar-flow hood. The initial coating experiments that were conducted with KDP used GR-651 polysiloxane resin, supplied precatalyzed as a 27.5% solution in butanol. Early results with this material indicated that it was too brittle in its fully cured state to withstand the mechanical stresses caused by the thermal expansion and contraction of KDP. Coatings prepared with this material were found to crack upon cooling after the bake cycle or when exposed to moisture. A potential solution to this problem was to use the uncatalyzed GR-650 resin, which was expected to be more flexible than GR-651 because of its lower degree of cure. This resulted in a lower glass-transition temperature for the polymer. The validity of this approach was confirmed by the successful spin deposition of an 0.8-μm film of GR-650 polysiloxane resin on a KDP substrate using a 3% solution of GR-650 resin in isopropanol. No cracking of the coating upon exposure of the coated KDP part to moisture was noticed. The interferometric quality of the KDP substrate, measured with a Zygo Mark II Interferometer at 633 nm, was unchanged by the presence of the coating.

2. KD*P

A sample of KD*P, 10 × 10 × 5-mm thick (95% deuterated) from Cleveland Crystals Co., which had been finished by diamond turning, was coated with a 3% solution of GR-650 polysiloxane resin in isopropanol under the same conditions used for the conventionally polished samples from Inrad. There appeared to be no appreciable difference in the behavior of KD*P and KDP toward the spin-coating technique used in the coating experiments.

3. Evaporative Thin-Film Overcoating of Polysiloxane-Coated KDP

Two Inrad KDP substrates that had been previously coated on one side with GR-650 polysiloxane resin were overcoated with a Ta_2O_3-SiO_2 multilayer evaporated thin film to produce a durable broadband AR coating. The AR coating was designed to accommodate the uncertainty in thickness of the polysiloxane layer. Prior to deposition of the thin-film coating, a small portion of the polysiloxane film near the edge of each sample was removed by rubbing with a cotton swab soaked in methanol. The exposed area on both samples was overcoated with a thin film of aluminum to aid in visualization of the KDP surface by Nomarski differential-interference contrast microscopy. One of the substrates was overcoated with the dielectric thin-film material, by e-beam evaporation at 150°C. Visual inspection of the overcoated KDP crystal after coating revealed a foggy texture over most of the coated surface, with the exception of some clear areas near the center of the piece. Detailed observation of the sample by Nomarski microscopy revealed that the fogginess was due to buckling of the polysiloxane underlayer (see Fig. 27.8) in a manner indicating high compressive stress. The polysiloxane/dielectric thin-film composite coating was exceptionally well adhered to the KDP substrate. The coating passed the "Scotch-tape" test and could only be removed with difficulty by scratching with a sharp knife. Attempts to remove the coating by wiping with a cotton swab soaked in methanol were unsuccessful. A second coating run at a lower temperature (100°C) was made. In this case no buckling of the polysiloxane underlayer was noted; however, the coating-to-substrate adhesion was considerably reduced, compared to the earlier high-temperature run. The coating was readily removed with the tape test. The surface quality of the dielectric thin-film polysiloxane-coated KDP substrate is revealed in Fig. 27.9. The surface roughness of the substrate appears to be reduced by the presence of the composite coating.

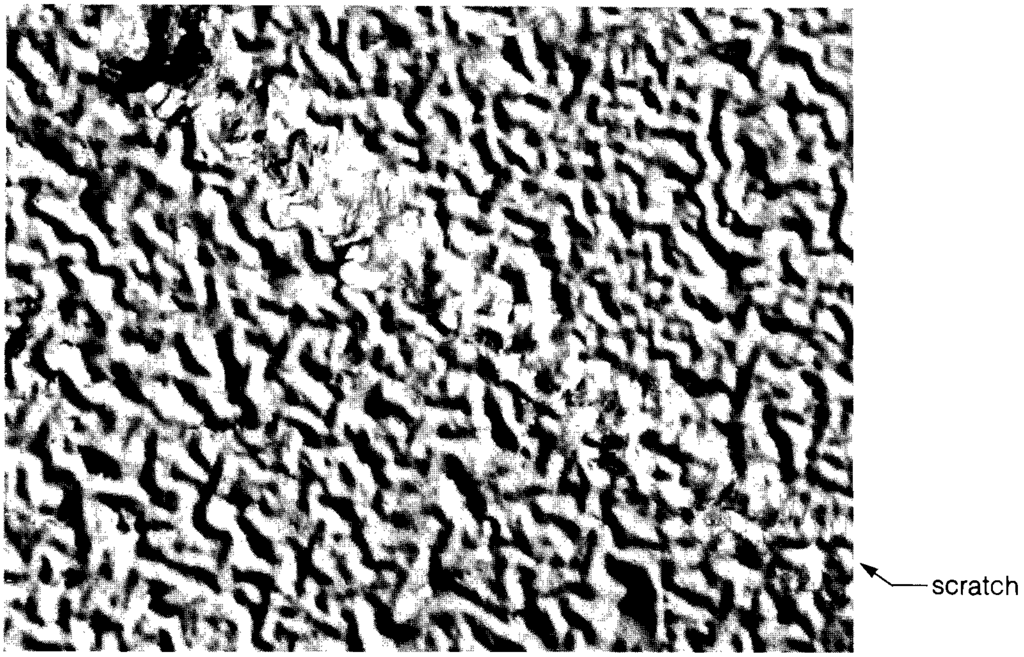

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Fig. 27.8
Polysiloxane-coated KDP overcoated with evaporated AR film at 150°C (magnification: 375x). The buckling of the polysiloxane underlayer is evidence of compressive stress caused by the high thermal expansion of the substrate at 150°C and the rigidity of the evaporated AR film. Adhesion of the composite film is excellent; the coating could only be removed with difficulty by scratching with a sharp knife.

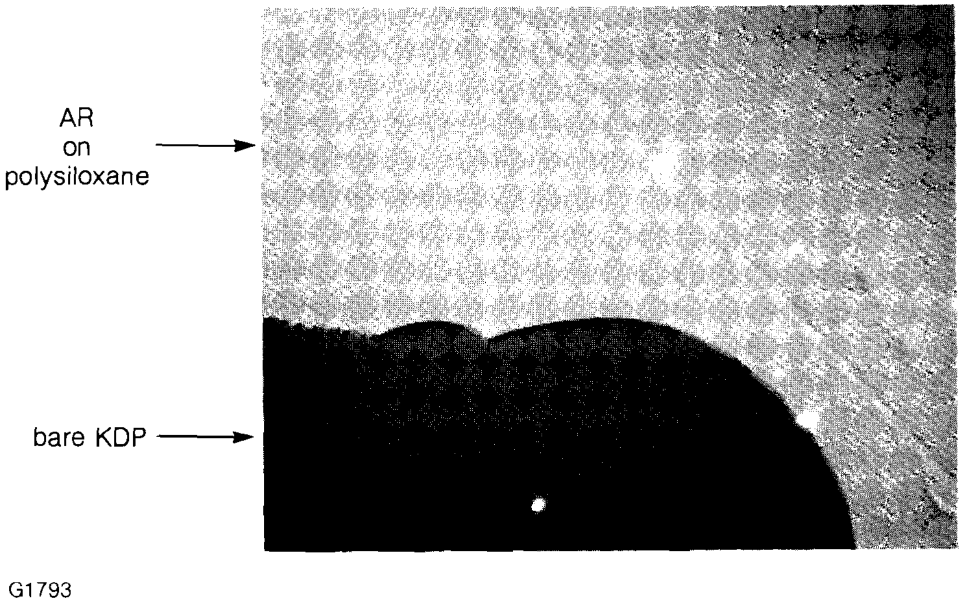

Fig. 27.9
Polysiloxane-coated KDP overcoated with evaporated AR film at 100°C. No buckling due to compressive stress is indicated. Adhesion of the composite film is poor. The area where the coating was removed by the "Scotch-tape" test is indicated in the lower portion of the photograph. A smoothing effect produced by the AR-PSX coating is evident (magnification: 750x).

4. Damage Testing Data: Coated KDP Samples

The coated samples of KDP and KD*P described earlier were subjected to some preliminary damage tests at 1064 nm. The results and experimental conditions for the tests are summarized in Tables 27.VI–27.VIII.

All of the polymer-coated samples displayed excellent damage test results, exceeding in some cases the damage threshold of the AR-coated BK-7 control. Application of the dielectric thin-film coating over the polymer coating, however, caused a substantial reduction in the damage threshold of the composite coating.

Table 27.VI
CW irradiation of GR-650 polysiloxane-coated KDP (tested at LLE).

Sample No.	1
Sample Description:	KDP, coated both sides with a 7-μm layer
Laser:	1-W cw Nd:YAG
Spot Size:	0.5 mm
Intensity:	400 W/cm^2
Irradiation Time:	10 min
Result:	no damage (100x microscopic observation)

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Table 27.VII
*Pulsed irradiation of GR-650 polysiloxane-coated KD*P (tested at General Electric Co.).*

Sample No.	2
Sample Description:	diamond-turned KD*P, coated on one side
Laser:	Nd:YAG, 1064 nm
Beam Size:	6 mm × 0.7 mm (measured with burn paper)
Pulse Width:	18 ns
Maximum Energy/Pulse:	240 mJ
Repetition Rate/Time:	5 KHz/1 min
Result:	no damage
Calculated Intensity	309 MW/cm^2
Calculated Fluence:	5.6 J/cm^2

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Table 27.VIII
Pulsed irradiation of dielectric thin-film polysiloxane-coated KDP (tested at Inrad).

Sample No.	3	
Sample Description:	KDP coated on one side with GR-650 polysiloxane resin, partially overcoated with a dielectric thin film	
Laser:	Nd:YAG (1064 nm)	
Pulse Width:	15 ns	
Number of Shots	100 per site, 6 sites per sample	
Results:	Material	Relative Damage Threshold
	AR-coated BK-7 control	1.0 (300 MW/cm^2)
	Polysiloxane-coated KDP	1.12
	Polysiloxane-dielectric thin-film-coated KDP	0.43

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Coatings for Lithium Niobate

To coat lithium niobate with a single-layer AR film, the refractive index of the coating material at 1064 nm must be 1.48, as calculated from the equation

$$n_1 = (n_0)^{1/2} , \qquad (1)$$

where n_1 is the index of coating and n_0 is the index of substrate. For lithium niobate, the average refractive index at 1064 nm is 2.1.

The particular polysiloxane resin selected for this task was GR-100 for the close match of its refractive index (1.49 at 589 nm) to the required value. The transmission characteristics of the GR-100 polysiloxane resin are similar to those of GR-650, demonstrating high transparency between 270 and 1800 nm with a slight increase in UV transparency after curing. The coating thickness required to produce a perfect AR effect at 1064 nm (zero-order interference) was calculated from the formula

$$\lambda_{min} = \frac{4n_1t}{2m+1} , \qquad (2)$$

where m is here 0, λ = 1064 nm, and n_1 = 1.48. The resulting value for the coating thickness (t) was 1800 Å.

Samples of lithium niobate used in the coating experiments were 10 × 10 × 2-mm thick plates provided by Inrad. Because of the unique physical properties of lithium niobate (the material is ferroelectric, piezoelectric, and undergoes temperature-induced surface charging) great care was required in handling, cleaning, and coating this material. As with the KDP coating experiments, all of the cleaning and coating operations were conducted in the horizontal laminar-flow hood under Class 100 clean-room conditions.

1. Coating Experiments: Lithium Niobate

Antireflective coatings formed from GR-100 polysiloxane resin were applied to the lithium niobate samples by spin deposition, using the procedure that was developed for KDP. The optimal solution concentration required to produce a polysiloxane coating of approximately 1800 Å was determined by spin coating three lithium niobate substrates with 3%, 6%, and 12% solutions of GR-100 polysiloxane resin in isopropanol and determining the transmission characteristics of the samples with the Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer. The results indicated that the 3% solids coating appeared to be the most likely candidate for producing a broadband AR coating at 1064 nm. One lithium niobate crystal was spin coated with the 3% solution of GR-100 in isopropanol and baked at 120°C for 24 hours to cure the coating. An additional substrate was coated on both sides with GR-100 polysiloxane resin by sequentially coating and baking each side of the substrate. In Fig. 27.10, the transmission characteristics of the single-side coated/baked, double-sided coated/baked, and uncoated lithium niobate samples are compared. A gain of about 8% in transmission at 1μm was achieved by coating one side; coating both sides of the substrate increased the transmission at 1μm to nearly 95%.

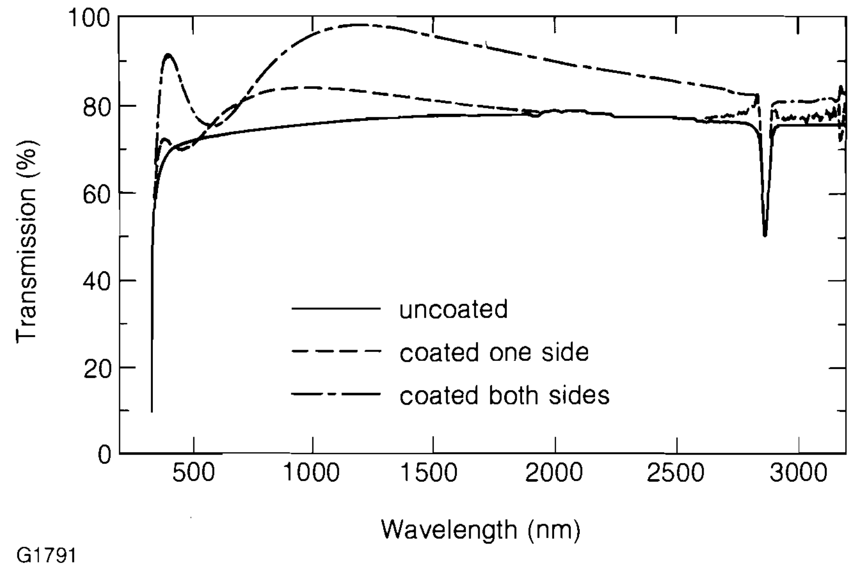

Fig. 27.10
Transmission spectra of polymer AR-coated lithium niobate samples and an uncoated control. Coating both sides increased transmission to nearly 95%.

2. Damage Test Data: Lithium Niobate

Damage testing of the polysiloxane-coated lithium niobate substrates was carried out at Inrad. As in earlier damage testing experiments with coated KDP, an AR-coated BK-7 substrate was used as a control sample and a relative damage threshold of 1.0 was assigned to the test results on this sample. The damage-test conditions and results are presented in Table 27.IX. The low damage resistance obtained for the polysiloxane-coated lithium niobate samples could be due to poor initial surface quality of the substrates before coating. It should be pointed out that although the laser-damage resistance of the GR-650 resin that was used for KDP coatings has been well documented, no data exists on the damage resistance of the GR-100 resin that was used in these experiments. Since an uncoated sample of lithium niobate was not available for damage testing, it was not possible to determine the degree of protection, if any, that was afforded by the presence of the polysiloxane coating.

Coatings for Potassium Pentaborate

Several samples of potassium pentaborate (10 × 11 × 5.5-mm thick) were received from Inrad for coating with a polysiloxane layer intended to protect the polished surfaces from degradation due to loss of lattice water to the environment. The samples had been polished on only two of the four narrow faces. One sample was left uncoated as a control; a second sample was prepared for coating by bonding a glass capillary tube to one of the narrow unpolished faces with an epoxy adhesive. The sample was secured by the capillary tube and was dipped in a 3% solids solution of GR-650 in isopropanol. After air drying, the sample was baked at 120°C for 24 hours. The coated and uncoated samples were photographed at 160x (Nomarski) to qualify the surface conditions

Table 27.IX
Pulsed irradiation of GR-100 polysiloxane-coated lithium niobate (tested at Inrad).

Sample Description	lithium niobate crystals, one piece coated on one side only, second piece coated on both sides	
Laser:	Nd:YAG (1064 nm)	
Pulse Width:	15 ns	
Number of Shots	100 per site, 6 sites per sample	
Results:	Material	Relative Damage Threshold
	AR-coated BK-7	1.00 (300 MW/cm^2)
	Goal for AR on LiNbO$_3$	0.63
	Polysiloxane-coated LiNbO$_3$ (1 pc, 1 side)	0.24
	Polysiloxane-coated LiNbO$_3$ (2 pc, 1 side)	0.26
	Polysiloxane-coated LiNbO$_3$ (2 pc, 2nd side)	0.30

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before exposure to the atmosphere (Figs. 27.11 and 27.12). The nodules that appear on the surface of the coated parts result from poor wetting of the KPB surface by the coating solution. The samples were placed in the laminar-flow hood, with the polished surfaces parallel to the laminar air-flow direction, and allowed to stand exposed to a constant flow of air for eight days. Examination of the samples under the microscope showed that the surface of the uncoated sample had become pitted (Fig. 27.13) and the coated sample was unchanged (Fig. 27.14). The experiment was continued for an additional six days and the pieces were reexamined. The uncoated piece had deteriorated to the point that the surface damage was visible to the unaided eye. The coated sample remained unchanged after a total of 14 days' exposure to the atmosphere.

The Owens-Illinois polysiloxane resins have been demonstrated to be potentially important materials for use as antireflective or protective coatings for certain nonlinear optical materials. Considerable effort involving the optimization of coating process conditions remains to be undertaken. One of the areas that requires attention is the optimization of dielectric thin-film deposition conditions for overcoating of polysiloxane-coated KDP to increase adhesion, improve optical quality, and increase the damage threshold of the composite coating. The effect of initial surface condition on the laser-damage resistance of polymer-coated lithium niobate crystals should also be investigated. For potassium pentaborate, optimum coating conditions and damage resistance of polysiloxane-coated substrates have yet to be determined. A natural extension of this work with polysiloxane resins would be the coating of urea and other nonlinear optical materials that have been difficult or impossible to coat by conventional means.

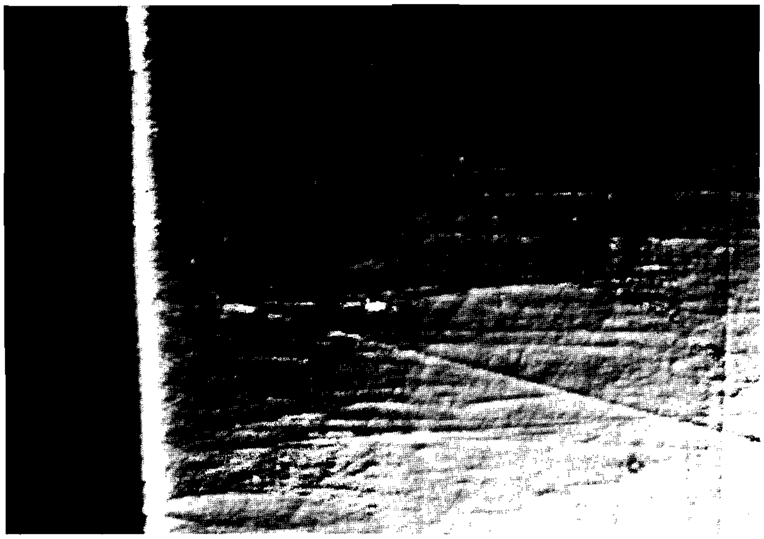
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Fig. 27.11
Uncoated potassium pentaborate control sample (magnification: 160x). Surface condition at the beginning of experiment. Surface scratches as a result of polishing are evident.

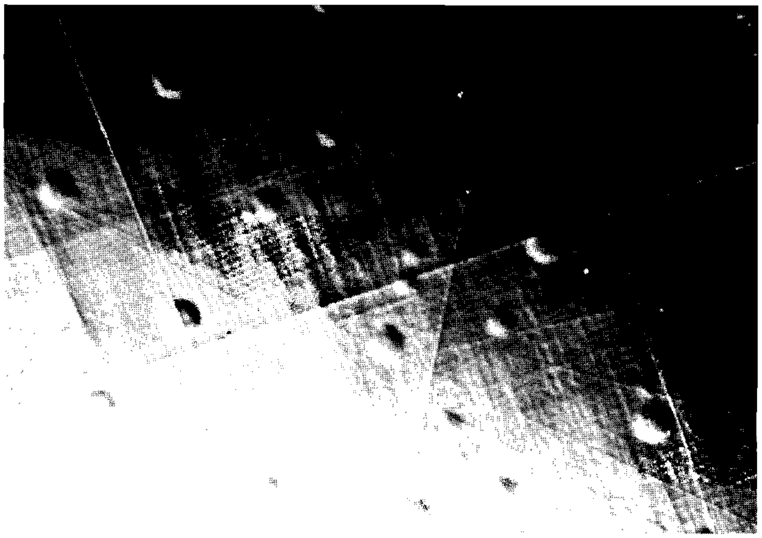
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Fig. 27.12
Potassium pentaborate sample dip-coated with a 3% solution of GR-650 polysiloxane resin in isopropanol. The photo indicates the surface condition at the beginning of experiment. Nodules, high spots in the coating, are due to poor wetting of the surface by the coating solution.

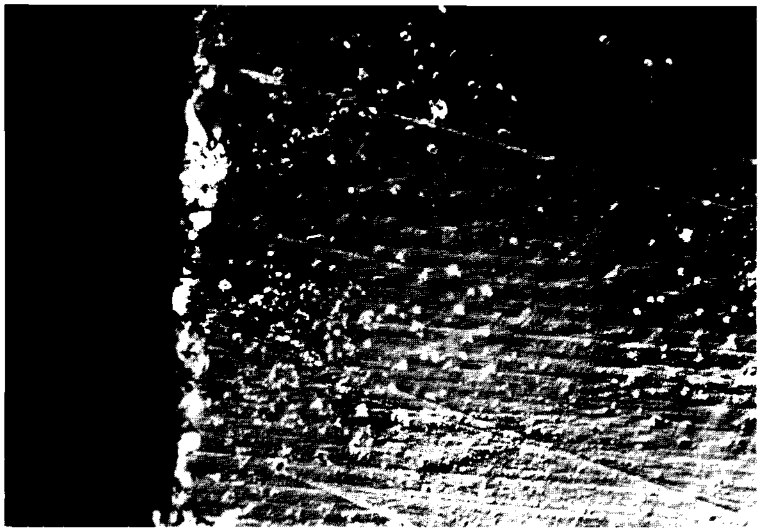
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Fig. 27.13
Uncoated potassium pentaborate control sample after eight days' exposure to air (magnification: 160x). The surface quality is considerably degraded due to loss of lattice water.

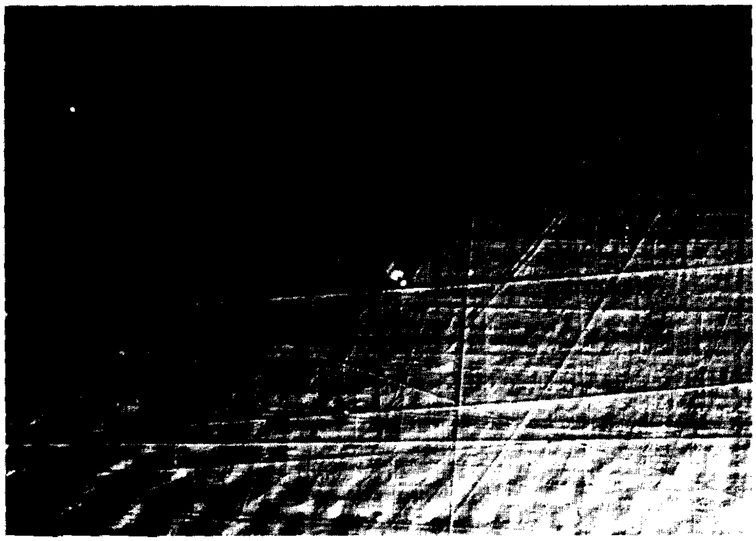

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Fig. 27.14
Coated potassium pentaborate sample after eight days' exposure to air (magnification: 160x). The surface quality is essentially unchanged, indicating the effectiveness of the polysiloxane coating as a moisture barrier.

ACKNOWLEDGMENT

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