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Processes for the Elimination of Fogging on KDP Crystals Prior to and During Use in Laser Systems*

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ABSTRACT

The rate of surface fogging on KDP crystals has been associated with several parameters in the diamond turning and subsequent cleaning process. Fogging can also occur during use because of environmental degradation. We have determined that reaction of the KDP surfaces with additives in the diamond turning oil has been a major factor in fogging and have found a replacement oil that eliminates this effect. We have also developed an antireflective silicone-sol coating that also reduces surface environmental deterioration during use by a factor of four.

1. INTRODUCTION

Potassium dihydrogen phosphate (KDP) crystals have been used as harmonic converters on the Nova laser at LLNL for over six years. The original converter arrays consisted of crystals whose surfaces had been prepared by wet diamond turning, cleaned and then coated with a single layer quarterwave antireflective (AR) coating of porous silica with a refractive index of 1.22.[1] This was prepared by a sol-gel process and was applied from colloidal suspension by spin coating at room temperature.

One factor influencing the conversion efficiency is environmental degradation or fogging of the crystal surfaces. While the atmosphere in the Nova laser bay is reasonably clean, there has been a steady decrease in performance over time due to fogging. Figure 1 shows the degradation of 0.35 μm light transmission over time for crystal arrays on six of the ten Nova beam lines. The time average rate of degradation ranged from 0.18 to 0.38%/month with an average of 0.28%/month.

Observations accumulated over the years have suggested that the fogging phenomenon is related to the machining oils to which the crystals were exposed during diamond turning and to environmental effects (humidity, air flow) during storage and use. During diamond turning the crystals are cooled and the machine is lubricated using a low molecular weight shower oil. The X-Y stage slides are lubricated using a high molecular weight way oil. During machining the heavy oil splashes into the light oil resulting in an approximately 2:1 mix of light:heavy oil ('mixed oil'). After diamond turning the crystals are cleaned at the manufacturer by a toluene dip and soak process. The crystals are again cleaned prior to sol-gel coating at LLNL using a toluene soak, dip, and 80 psi spray process. While on the beamline, the crystals are exposed to ambient temperatures and relative humidities of < 50%.

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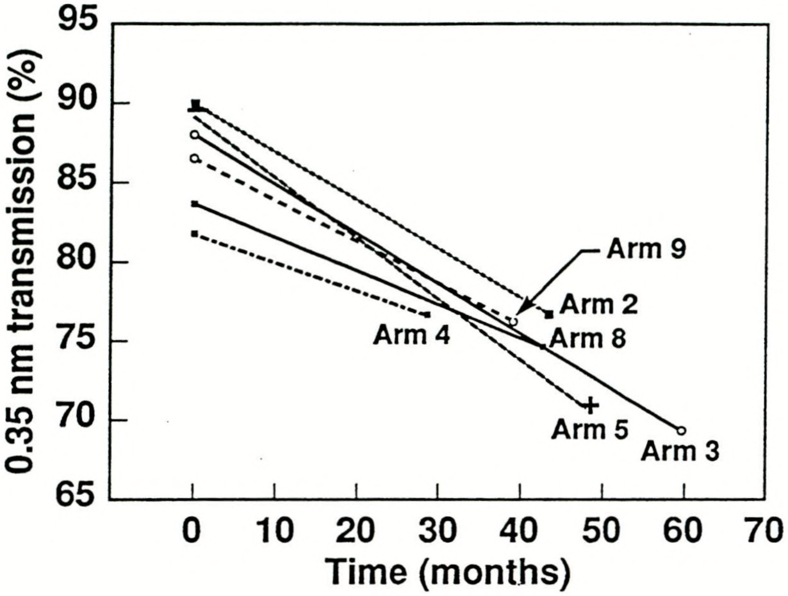

Fig. 1. Plot of 0.35 μm transmission degradation through the frequency conversion arrays on six of the Nova laser beamlines.

The fogging of the crystals is very sensitive to the environment. Some crystals have been kept on desks for years without fogging, while others have fogged overnight when stored in a fume hood. Condensation of water vapor onto the crystals will surely cause some surface degradation. Fogging degradation generally appears as a haze on the surface. Under light microscopy the fog often appears to consist of micron scale scatter points. Under the higher magnifications of electron microscopy the fogging takes many forms. In most cases the fogging features appear as rough cylindrical particles of ~ 3 μm in length.[2] Other structures observed include what appears to be a dendritic growth. The range of structures associated with KDP crystal fogging suggests that several mechanisms are responsible for this degradation process.

Chemical handbooks appear to be split as to whether KDP is hygroscopic but it does have a high solubility in water. The confusion over its hydrophilic properties is probably related to a strong dependence of surface reactivity on surface contamination and structure.

The reactivity of KDP to atmospheric water has been demonstrated by Hirsch and Adams.[3] They showed that when a KDP surface was damaged by ion bombardment in vacuum the surface was made reactive. Upon bringing the crystal to ambient conditions the surface would react with water vapor producing a "corrosion" reaction. Their description of "rod-like" corrosion products with micron-scale lengths agrees with our observations on diamond turned crystals. Hirsch's work suggests that a perfect KDP surface is not reactive to atmospheric water but that the surface can be activated by structural damage.

We are now in the process of replacing all the old KDP arrays with new arrays. Crystals in these arrays have been prepared, cleaned and coated according to techniques gleaned from our experiences over the last few years. This paper summarizes these experiences and describes our new process.

2. CONTROLLED FOGGING TESTS

Initial experiments were designed to determine if humidity and machining oils did in fact influence crystal fogging rates. The first set of experiments tested six 1-in. square crystals that were diamond turned at LLNL using either the show, way, or mixed oil (2 crystals each). After diamond turning the samples were dip cleaned in toluene and stored in a clean room under high air flow. The cleaning method was a scaled-down version of that used in the manufacturing process. Prior to storage the crystals were examined visually using bright-light illumination and using 50X and 107X Nomarski microscopy. Polaroid photography was used to document the state of the crystal surface during the tests. No sign of fogging was present on the crystals initially. The crystals were then reexamined using Nomarski microscopy after periods of one week. The observations made over a period of 6 weeks are shown in Table 1. The relative degrees of fogging reported are based on the apparent density of artifacts on the crystal surface. The fogging rates are too slow to produce measurable changes in transmission during the test period. No fogging was observed on any of the crystals after 1 week. After 3 weeks samples machined in shower oil were fogged. Also, one mixed oil sample showed some fogging. After 5 weeks the two way oil samples showed some minor fogging. Shower oil samples showed the heaviest fogging during all stages of the test. Fogged crystal surfaces from these tests consisted of 3-6 μm-size raised structures on a smooth background. The density of these features was about 1000/cm^2. These tests indicated that the shower oil produced the highest rate of KDP surface fogging.

Another set of crystals was prepared in order to determine the influence of humidity on the fogging rate. Four 1-in. square samples were diamond turned in the mixed oil and one sample was turned in the shower oil. The samples were dip cleaned in toluene and then examined as in the oil comparison tests above. The crystals were then stored in chambers with humidity levels of 80%, 44%, and 0% RH. These chambers were glass desiccators containing saturated solutions with the appropriate vapor pressures.[4] Two mixed oil samples stored at 80% RH were fogged after 3 days. Fogging did not get much worse after an additional two weeks. Mixed oil samples stored at 44% and 0% RH had not fogged after two weeks. The sample diamond turned in shower oil and then exposed to 80% humidity showed the highest degree of fogging after only one week. At magnifications of 100X the fogging had an 'orange peel' morphology. At 440X the fogging appeared to be many small 'bumps' about 5-10 μm in diameter.

Oil test:		**1 week**	**3 weeks**	**5 weeks**
	Shower	—	●	⬤
	Way	—	—	•
	Mixed	—	·	•
Humidity test: **(% RH)**		**1 week**	**3 weeks**	**5 weeks**
Mixed	**80%**	●	●	●
	80%	●	●	●
	44%	—	—	—
	0%	—	—	—
Shower	**80%**	⬤	⬤	⬤

No fogging — · • ● ⬤ **Heavy fogging**

Table 1. Table showing the relative amounts of fogging observed during controlled fogging tests on freshly diamond turned KDP crystals.

One additional sample was diamond turned in the mixed oil and then left immersed in oil for over 20 hours. This sample was then dip cleaned in toluene. The side of the crystal not facing the chuck was heavily fogged. One edge of the crystal showed extra heavy fogging. The latter observation may be due to a large bead of oil formed at the bottom edge of the crystal as the oil drains. The side facing the chuck showed little or no fogging. The fogging morphology was similar to that observed in the oil/humidity tests.

The tests described above indicate that the fogging rate is influenced by the diamond turning oils with the highest fogging rate being observed for the shower oil. Accelerated fogging at high humidity levels shows that water is a key reactant in the fogging process.

3. CHEMICAL ANALYSIS OF DIAMOND TURNING OILS

GC analysis of the oils showed that the shower oil and the way oil both contained a wide molecular weight band of hydrocarbons and that the band for the way oil was ~ 35% heavier than was the shower oil. These pure hydrocarbons should not react with the KDP crystals. The oils did, however, contain a number of additives. The shower oil contained an oxidation inhibitor (metal salts), a pour-point depressant (polybutene), and an anti-wear agent (nitrogen based), while the way oil contained an antiwear agent (silicone based) and a tackiness agent (rubber). Inorganic analysis of the oils showed that the major components of the oxidation inhibitor were organic salts of Zn, Ca, and P.

The surface of KDP consists essentially of -P-O-H groups and should behave chemically similarly to phosphoric acid, H_3PO_4. We therefore qualitatively tested the reactivity of the oils to phosphoric acid. 20 ml of the way and shower oils were added to separate vials containing 20 ml of H_3PO_4. As the oil and acid are immiscible, the mixture was stirred for two days and then separated using a centrifuge. The separated acid showed an obvious change in color for both oils. For the way oil the acid was light yellow while for the shower oil the acid was dark brown. A pure mineral oil was also mixed with the acid. The pure oil showed little or no reaction with the acid. This test therefore suggested that it was the additives in the oil that were reactive to the KDP surface.

We also carried out a test in which the shower oil was stirred with powdered KDP for 24 hours. Quantitative analysis of the oil before and after the stirring indicated that the calcium content had been reduced from 109 ppm to 81 ppm and zinc from 560 ppm to 368 ppm. These results show that Zn and Ca are leached from the oil by KDP. It is likely that these metals form phosphates on the surface by reaction with the free acid groups. Both calcium and zinc phosphates are known to form hydrates which could contribute to the fogging problem.

As a result of these tests a pure mineral oil is now used to diamond turn KDP crystals for the Nova laser system. The change of oils has noticeably reduced the occurrence of fogging on freshly turned crystals.

4. INFLUENCE OF SURFACE STRUCTURE

Part of the nonreproducibility of fogging experiments is likely related to a dependence on surface properties. Fogging rates for controlled tests were greatest when freshly turned surfaces were exposed to humid environments. The fogging rate was much slower for crystals that were exposed to ambient conditions for several days prior to exposure to humidity. We propose that the absorption of contaminants at reactive sites may slow the fogging reaction.

The fogging rate is also dependent on surface roughness. Fogging was often most significant along diamond turning lines or scratches. The fogging made these features much more visible and may therefore contribute to degradations in beam uniformity caused by diamond turning artifacts. In some cases beam modulations from the crystal surface have been significant enough on the Nova system that optics downstream from the crystal have shown laser damage patterns that match the KDP diamond turning patterns. Hirsch and Adams[2] also reported increased corrosion at scratches and attributed this to high concentrations of catalytically active sites at surface irregularities.

The fogging rate was also dependent on the direction of diamond turning tool movement relative to crystallographic orientation. Two KD*P (KD_2PO_4) crystals were cut with surface planes parallel to the crystal z-axis. For one crystal the surface was diamond turned with the tool motion perpendicular to the z-axis, while for the other crystal the tool moved parallel to the z-axis. For two pairs of crystals the sample turned parallel to the z-axis showed a higher rate of fogging.

5. CLEANING OF DIAMOND TURNED KDP CRYSTAL

KDP crystal cleaning procedures have been developed in order to maximize the removal of diamond turning oils which influence fogging and also to remove contaminants which affect AR coating quality. The cleaning procedures consist of several stages of dipping, drag wiping, and spraying with toluene as listed below:

Cleaning process immediately following diamond turning:

1. Blot oil off surface with lens tissue.
2. Dip crystal into three successive toluene tanks.
3. Place plastic film wrap on crystal, smooth wrinkles, and then remove. Repeat on other side of crystal. This process removes KDP dust and aluminum chuck residues.
4. Blow crystal dry with N_2 treated with an anti-static gun. The anti-static gun reduces static charge on the crystal surface.
5. Drag wipe with toluene.
6. Remove remaining residues with cotton swabs.
7. Toluene dip soak crystal for 10 minutes.

After drying, the crystals are vacuum bagged for shipment. The vacuum bagging reduces the influence of humidity on the crystals during shipment and storage.

Cleaning process upon receipt of crystals at LLNL:

1. Toluene soak for 16 hours. Check for sheeting on surface during removal. Solution sheeting is required for good coating adhesion.
2. 80 psi spray with toluene.
3. Drag wipe with toluene soaked lens tissue.
4. Soak for two hours in toluene. Check for sheeting during removal.
5. Repeat steps 2 and 3.

We attempted to substitute tetrachloroethylene for toluene in the cleaning process at LLNL. This change in solvent resulted in accelerated hazing of the crystals. It was determined that the tetrachloroethylene decomposes during storage to form trace amounts of HCl. The acid reacts with the amphoteric KDP resulting in a type of fogging. In contrast to the other types of fogging discussed above, the tetrachloroethylene fogging could be removed by recleaning the surface with toluene. The fogging particles in this case were likely KCl crystals.

6. COATING OF KDP

The KDP crystals in the old arrays, with one exception, were coated only with a sol-gel SiO_2 single layer AR coating.[1] This SiO_2 coating was not expected to provide effective environmental protection because of its porosity. The one exception was a crystal that was undercoated with a methyl silicone prior to the application of the porous silica overcoat. The silicone was dense and was expected to give some environmental protection and this indeed turned out to be the case. The transmission loss at 355 nm, described earlier, was reduced from 0.28%/month to 0.06%/month and much of the loss could be regained by spray cleaning with toluene. This early result encouraged further investigation which is described below.

7. PROTECTIVE COATING REQUIREMENTS

There are several essential properties that a potential protective coating material must have if it is to be used on KDP harmonic converter crystals in a high power laser:

1. High transmission at the conversion wavelength.
2. Adequate laser damage threshold.
3. Application method that is compatible with the fragile nature and temperature sensitivity of KDP.
4. Compatibility with any optical overcoating that might be used later.

Items 1 and 2 more or less rule out all conventional organic polymers especially if required for 265 nm or 355 nm wavelengths. This restricts the field considerably, but materials such as methyl silicones or fully fluorinated polymers remain likely candidates. We have evaluated one of each of these classes of materials and have found that both give good results. The silicone turned out to give better performance and our evaluation is described below.

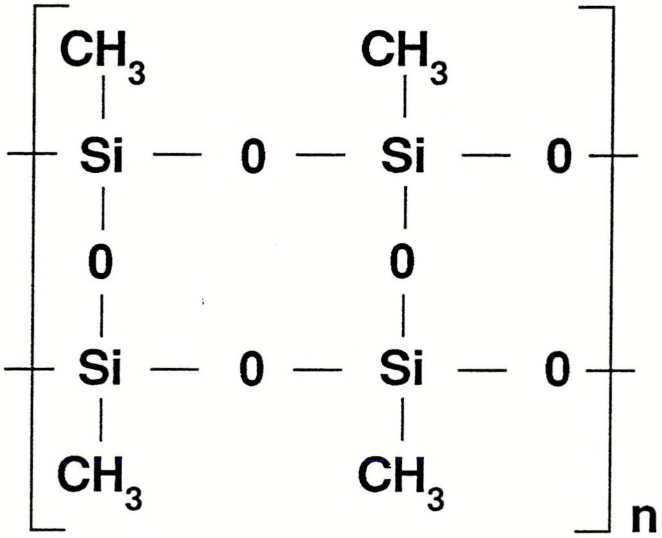

Fig. 2. Idealized structure of cured GR 654L.

8. METHYL SILICONE

The methyl silicone that we chose for evaluation is a commercial material manufactured by Owens-Illinois Inc., Toledo, Ohio under the trade name Glass Resin GR 654L.[5] One of its major uses is a scratch resistant coating for plastic window materials such as polycarbonate and polymethylmethacrylate. As such it has shown high transparency and weather, i.e. UV, resistance.

The material is a high purity product prepared by the hydrolysis of methyltrimethoxy silane and is supplied as a soluble prepolymer in ethanol solution. It is applied by spin or dip and, after cure for 16 hours at 135°, gives a hard, dense, transparent and insoluble coating whose structure is shown in an idealized and simplified form in Fig. 2. The application method, solvent system and cure are all quite compatible with KDP. The refractive index of the cured coating is 1.41 and it therefore has antireflective properties when applied to KDP (index 1.49-1.51). This is sufficient to reduce reflection from 4% to 2%

per surface. We, however, would like to improve this optical performance by overcoating with our porous silica AR material. This porous silica coating will henceforth be referred to as the "sol" coating because it is prepared from a colloidal suspension or "sol" of silica. Our theoretical calculations indicated that this two layer system would give a broad transmission increase which could be arranged to cover two harmonics by a suitable choice of coating thicknesses. A typical KDP array, operating as shown in Fig. 3 has surfaces exposed to different wavelengths requiring different AR coatings. Calculations showed that this could conveniently be accomplished by dip coating all crystals in silicone (i.e., same coating thickness both sides) and then spin or dip coating porous silica on top at a thickness dependent on the surface AR requirements. The transmission curves shown in Figs. 4 and 5 show how this can be done. In theory then it should be possible to obtain near zero reflection for all surfaces. This is much better than the compromise coating that we had previously been using for the two inner surfaces of the KDP array, the transmission curve for which is shown in Fig. 6. The single surface reflection is 1.1% at the two wavelengths.

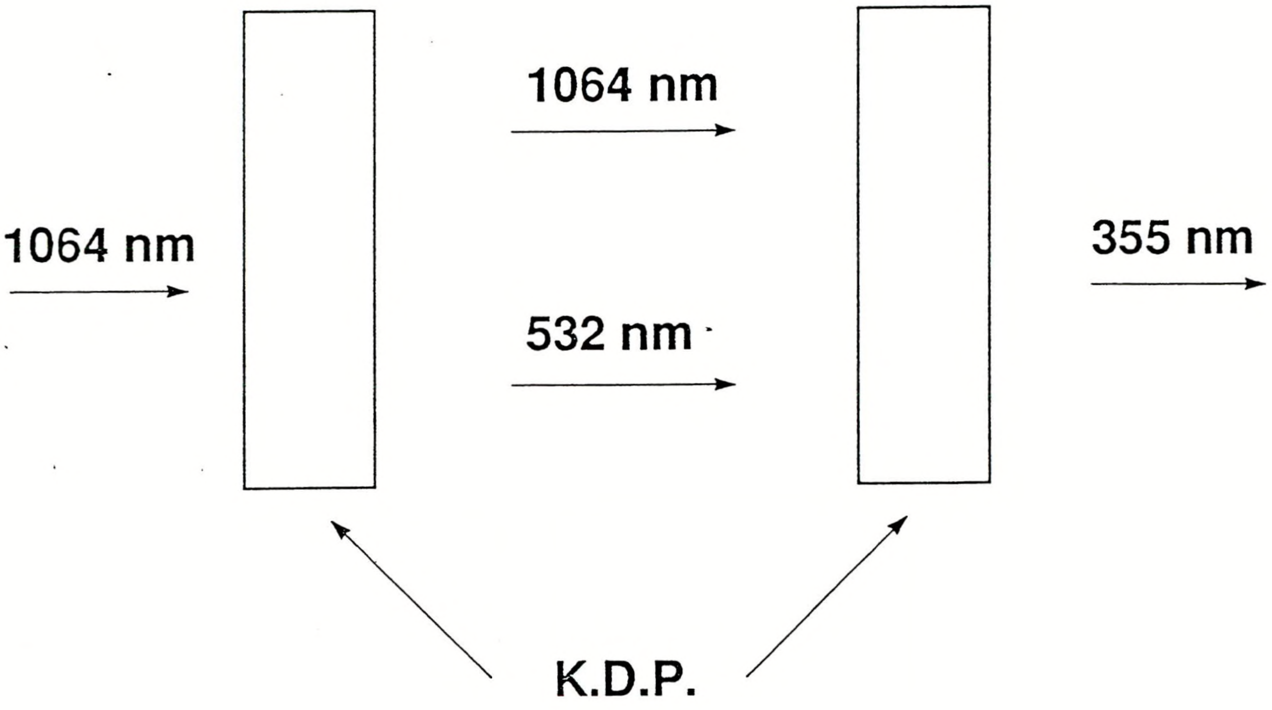

Fig. 3. Wavelengths in typical KDP converter array.

9. EXPERIMENTAL

9.1 GR 654L solution

Owens-Illinois GR 654L solution was received as an ethanol solution containing 40% solids. The material was diluted with twice its weight of anhydrous ethanol and then filtered through a 0.2 µm polyfluorocarbon filter.

9.2 Silica suspension

The colloidal suspension of silica was prepared by the ammonia catalyzed hydrolysis of tetraethylsilicate in ethanol by the method previously described.[1] Suspensions containing the equivalent of 3% SiO_2 were refluxed for 24 hours to remove ammonia and then filtered through a 0.2 µm polyfluorocarbon filter.

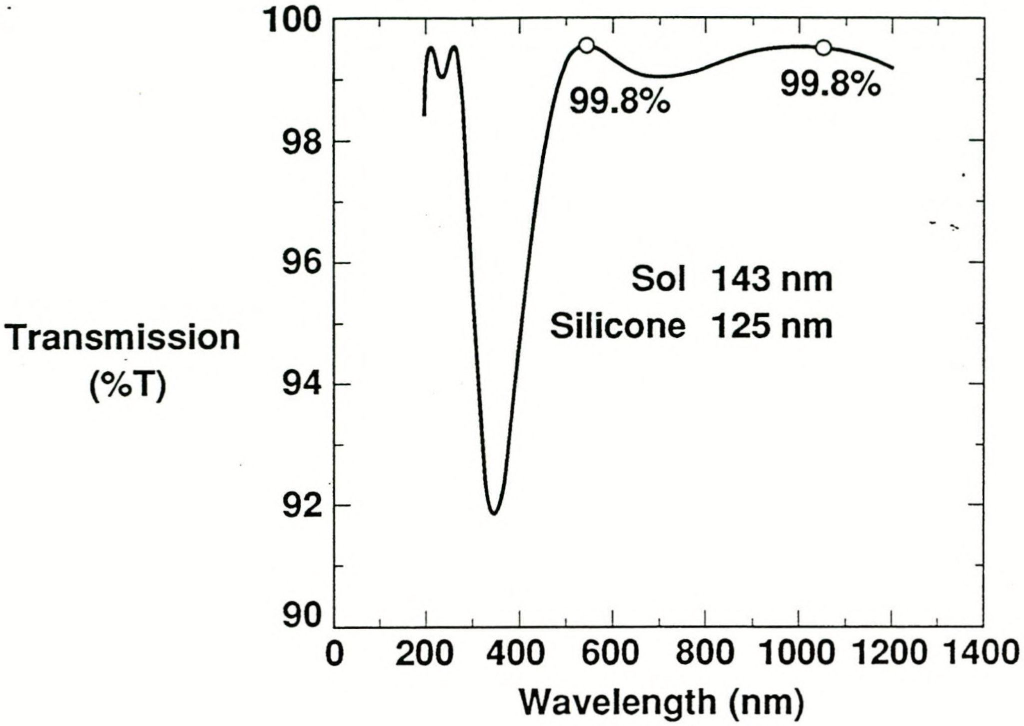

Fig. 4. Theoretical transmission of two layer coating for use at 1064 nm and 532 nm.

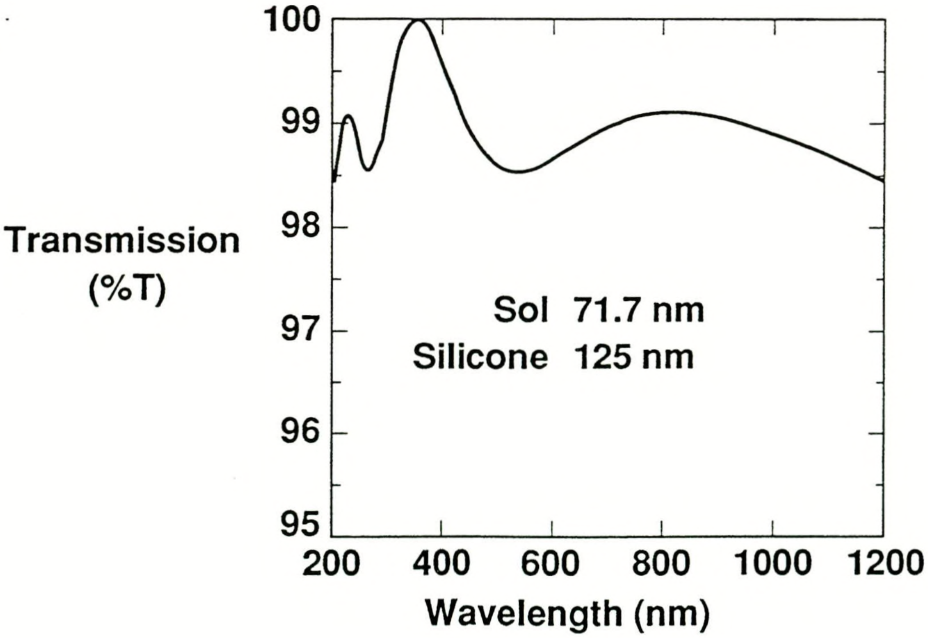

Fig. 5. Theoretical transmission of two layer coating for use at 355 nm only.

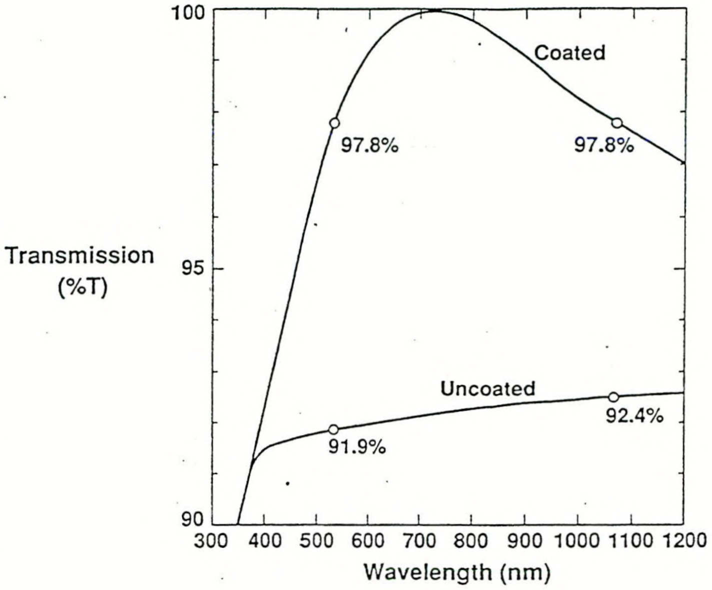

Fig. 6. Theoretical transmission of compromise coating for 1064 nm and 532 nm.

9.3 Substrates

Coating was carried out on KDP substrates which were either 5 cm x 5 cm x 1 cm or 27 cm x 27 cm x 1.5 cm (Nova size). All samples had diamond-turned surfaces and were rigorously cleaned in toluene prior to coating.

9.4 Coating procedure

Samples were either dip or spin coated in a class 100 clean room. All silicone coatings were prepared by dip coating and the withdrawal rate was adjusted to give true thickness of 125 nm after cure. This thickness is the theoretical thickness for the optimum optical performance described earlier. Cure was carried out by heating the substrates in a ventilated box in a forced air oven to 135° over a period of 8 hours. This temperature was held for 16 hours and the samples then cooled in the oven without removal from the box.

Two thicknesses of sol overcoat were required depending on the position of the sample in the array. The first crystal required 143 nm of sol for the broadband AR coating to be effective at 1064 nm and 532 nm. This was deposited by dip coating. The second crystal required an AR coating for 355 nm on the exit surface and 532 nm and 1064 nm on the inlet. This was accomplished by dip coating 71.5 nm of sol on both sides first and then spin coating another 71.5 nm of sol on one side only (inlet surface).

9.5 Damage threshold measurements

The damage thresholds of all samples were measured on our Nd:YAG Reptile facility[6] using a spot size of about 1-2 mm diameter. Measurements were carried out at two different wavelengths, 1064 nm and 355 nm, with a pulse length of 10 ns. Usually 600 shots were applied to a single spot at a repetition rate of 10 Hz. Two types of measurements were made, conditioned and unconditioned. Unconditioned samples received all shots at one fluence at one site, if no damage was observed the fluence was increased and more shots applied to a new site. This was continued until damage was observed. Conditioned sites received shots with the fluence ramped from near zero to the desired maximum. If no damage was observed this was repeated on a fresh site to a higher maximum until damage was observed.

Damage was defined as any permanent alteration in the coating observable using a Nomarski microscope in bright or dark field at up to 400X magnification.

10. DISCUSSION OF COATING RESULTS

10.1 Transmission

The transmission curves for a KDP crystal to be used at 532 nm and 1064 nm which was first coated with silicone and then with sol are shown in Fig. 7. Several points are of note. The uncoated curve shows that there is about 5% absorption by the crystal at 1064 nm. There is also some scatter loss below 400 nm probably due to diamond turning lines on the surface. The silicone coating gives a typical quarterwave AR transmission curve with a maximum at 710 nm and the corresponding minimum at 355 nm. This minimum should touch the uncoated curve because this is the halfwave point but there is probably a decrease in scatter, and hence increase in transmission, due to the smoothing effect of the silicone. Finally, the broadband effect of the sol overcoat is well illustrated and gives a 7.0% and 6.5% increase in transmission to surfaces at the two wavelengths of interest. This is close to what we expect from the theoretical calculations described earlier.

The corresponding transmission curve for the KDP surface to be used at 355 nm is shown in Fig. 8. As 355 nm is the halfwave point for the silicone coating, it has no optical effect at this wavelength. Increase in transmission is therefore due solely to the sol coating and thus came out at 7.6%. The sol coating by itself normally gives near zero reflection and the loss here again may be due to a little scatter.

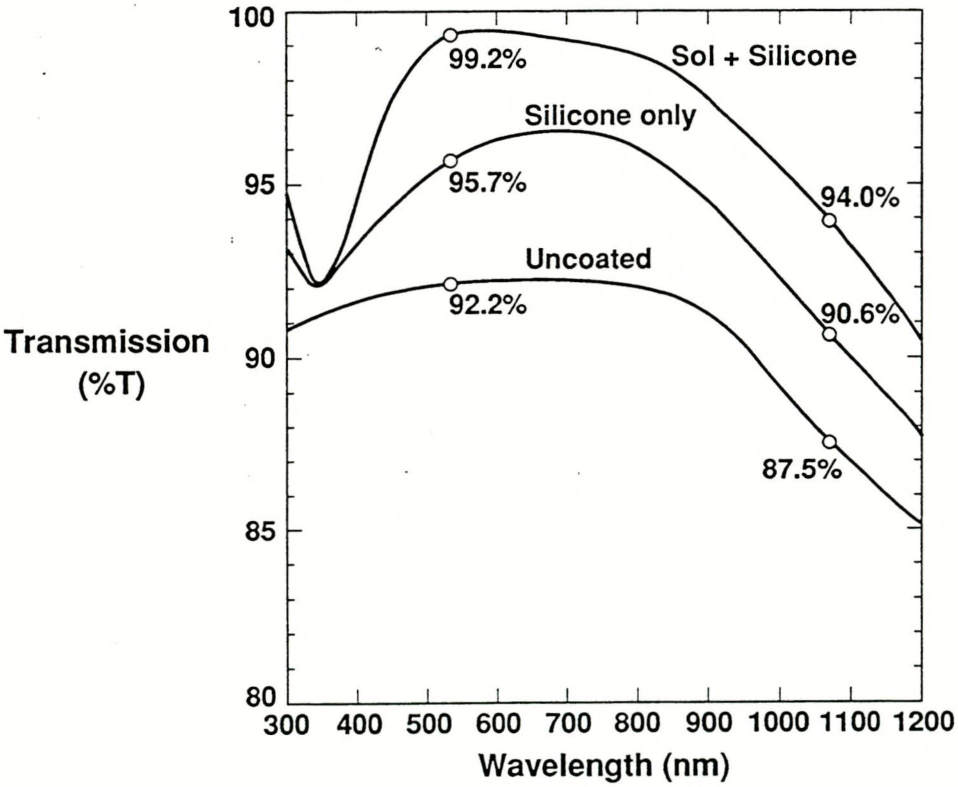

Fig. 7. Transmission curves for KDP coated for 532 nm and 1064 nm.

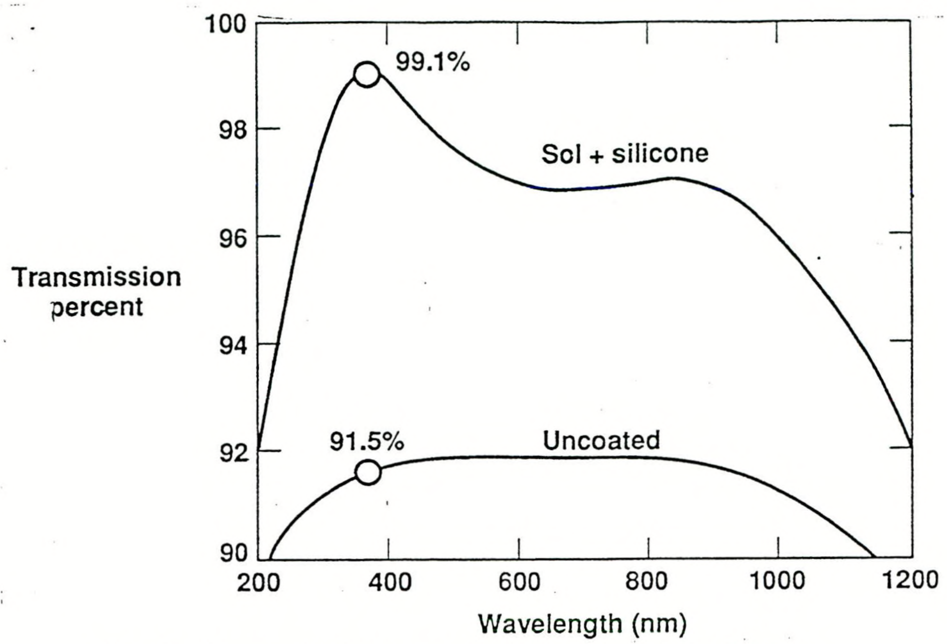

Fig. 8. Transmission curve for KDP coated for 355 nm.

10.2 Damage thresholds

The damage thresholds for the sol-silicone coating, with bare surface KDP levels for comparison, are shown in Table 2.

Sample	1064 nm / 10 ns	355 nm / 10 ns
Sol-silicone	> 40 J/cm^2	20 J/cm^2
Bare surface KDP	> 40 J/cm^2	20-30 J/cm^2

Table 2. Damage threshold levels of coated and bare surface KDP.

All levels reported are for conditioned samples although we found that there was little difference between conditioned and unconditioned values for the coated samples. In contrast, conditioned values were always higher for bare surface KDP. Damage of the coated surface was in all cases minor at the reported fluences and did not become massive until considerably higher values were reached. At 1064 nm the threshold of the coated sample is comparable to bare surface. We have not quoted exact values because bulk damage becomes significant at these levels and it is sometimes difficult to identify surface damage. At 355 nm the bare surface KDP is definitely superior to the coated sample.

These damage threshold results together with the optical properties were considered to be good enough to justify coating all the new arrays with this system.

11. ENVIRONMENTAL

The protective effect of dense optical coatings on a sensitive substrate is hindered by the thinness of the coating necessitated by its optical requirement. Our silicone coating is only 125 nm thick and this thickness is not sufficient to stop fairly rapid diffusion of low molecular weight vapors, such as water, through the film which can still be detrimental to the substrate. The coating can be a liquid barrier, however, and we found that a coated KDP sample (which is highly water soluble) could be briefly sprayed with a jet of water from a wash bottle with no effect. The water just beaded up and flowed off.

We did not set up any specific environmental test to evaluate the protection given to coated samples, if any. However, we do have the results of our prototype sol-silicone system used on the Nova which was described earlier. This gave a considerable reduction in the rate of transmission loss over the long term. Our current tests with the coating of the whole array should confirm this.

12. SUMMARY

We have developed improved processes for surface finishing, cleaning and coating KDP crystals used in harmonic converter arrays. These improvements can be summarized as follows:

(a) The conventional diamond turning oil, which contains additives, was replaced with an additive-free high purity mineral oil. Metallic additives in the conventional oil were shown to react with the KDP surface to give products that enhance environmental instability.

(b) A rigorous cleaning process was used to ensure complete removal of oil residues and surface debris. This involved a toluene soak and high pressure spray for the oil and the use of plastic sheet wrap as a contact adhesive for the particulate debris.

(c) Crystals were finally coated first with a dense methyl silicone for environmental protection and then with porous silica for antireflection.

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