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Optical and Environmentally Protective Coatings for Potassium Dihydrogen Phosphate (KDP) *Harmonic Converter Crystals*

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Optical and Environmentally Protective Coatings for Potassium Dihydrogen Phosphate (KDP) Harmonic Converter Crystals*

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ABSTRACT

Potassium dihydrogen phosphate (KDP) crystals have been used as harmonic converters on the Nova laser at LLNL for over six years. All crystals were coated with a single layer, quarterwave AR coating of porous silica with a refractive index of 1.22. This was prepared by a sol-gel process and was applied from a colloidal suspension by spin coating at room temperature. A few crystals were also coated with a methyl silicone coating prior to the application of the AR coating for environmental protection. The initial optical performance of all crystals was very good but there has been some deterioration over the years because of environmental and laser damage degradation. The deterioration in the silicone samples was, however, much less than the others. We are now in the process of replacing all ten KDP arrays with new crystals and will apply the silicone undercoat to all samples.

Recently we have been evaluating a new perfluorinated organic polymer coating which has a refractive index of 1.29. This material is soluble in fluorinated solvents and can be applied by dip coating from solution at room temperature. We hope that this can provide environmental protection when applied to KDP and also act as an AR coating at the same time. The optical performance is not as good as our porous silica because of the higher index; about 0.3% reflection per surface is obtained.

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1. INTRODUCTION

Potassium dihydrogen phosphate (KDP) crystal surfaces are acidic and subject to environmental contamination on exposure to the typical operating atmosphere. This contamination can lead to fogging because of laser damage and possible water absorption. Loss in transmission and therefore conversion efficiency then follows.

The Nova laser at Lawrence Livermore National Laboratory uses KDP arrays as harmonic converters. The crystals in these arrays are coated with a sol-gel porous silica quarterwave antireflective (AR) coating(1) which, while optically very good, provides no environmental protection for the KDP surface. While the atmosphere in the laser bay is reasonably clean, there has been a steady decrease in performance over time due to fogging. We are now in the process of replacing all the arrays with reconditioned KDP and are using a two layer coating system which provides environmental protection as well as excellent optical performance. One small section of one array was coated with a prototype of this two-layer system in 1984 and has shown encouraging results. The rate of transmission loss due to fogging was reduced by a factor of about three when compared with the standard single layer AR-coated material.

In this paper we will first list the requirements for a protective coating for KDP and discuss some of the potential candidates. We will then describe the two layer coating system that is now being put on the KDP in the Nova laser. Finally, an alternative single layer coating which serves both as a protective and optical coating, which we have also briefly investigated, will be discussed.

2. 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 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. Our evaluation is described below.

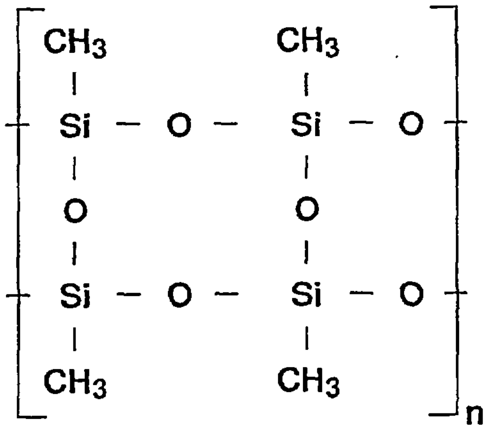

Fig. 1. Idealized structure of cured GR654L.

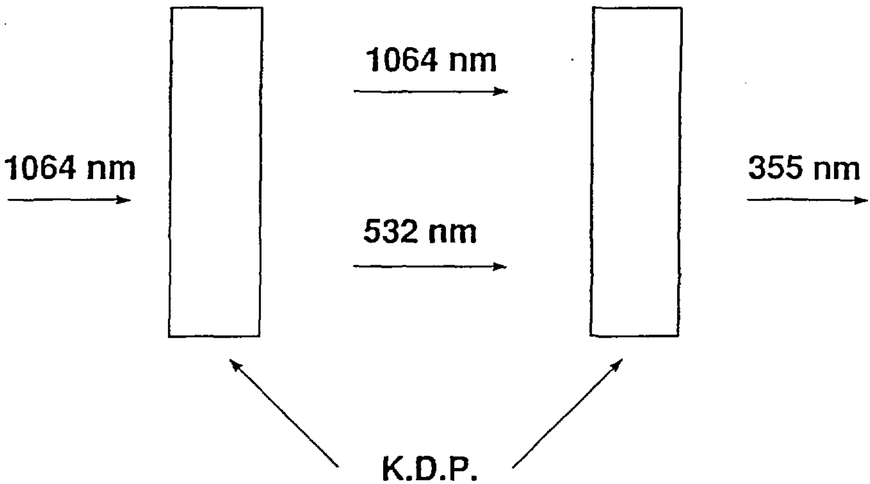

Fig. 2. Wavelengths in typical KDP converter array.

3. 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.[2] One of its major uses is as 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.

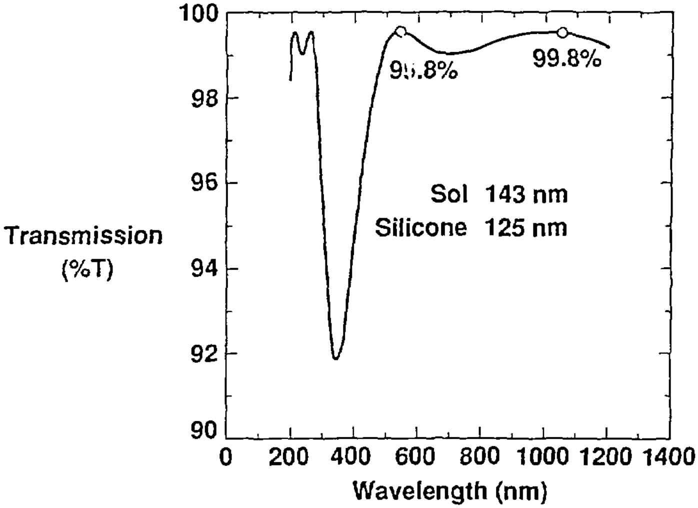

Fig. 3. Theoretical transmission of two layer coating for use at 1064 nm and 532 nm.

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. 1. 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 thickness. A typical KDP array, operating as shown in Fig. 2, 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. 3 and 4 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 this is shown in Fig. 5 in which the single surface reflection is 1.1% at the two wavelengths.

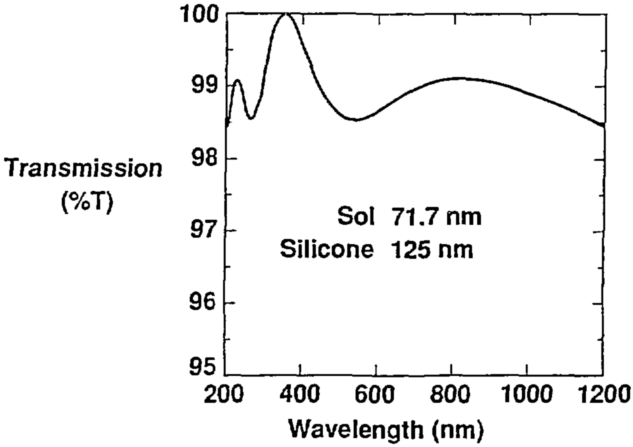

Fig. 4. Theoretical transmission of two layer coating for use at 355 nm only.

4. TEFLON AF 2400

We have also investigated a system which incorporates both environmental protection and optical performance in a single coat. The coating material is a commercial product manufactured by the DuPont Company under the trade name Teflon® AF 2400.[3] This is a random copolymer of tetrafluoroethylene (15 mole %) and 2,2, bis-trifluoromethyl, 4,5 -difluoro, 1,3 dioxole (85 mole%). Its structure is shown in Fig. 6. Like other fluorocarbon polymers, for example poly-tetrafluoroethylene or Teflon®, it is fully fluorinated and contains no hydrogen. Unlike other fluorocarbon polymers it has some room temperature solubility in fluorine containing solvents, is amorphous and non-absorbing down to 200 nm. The transmission of a 1 mil. free film is shown in Fig. 7; it also has the lowest refractive index of any known solid material (1.29). Because of the solubility, coatings can readily be prepared from solution by any of the usual methods. On substrates with refractive index about 1.5 somewhat inferior optical performance might be expected because of the high index. For example, with KDP, a reflection of about 0.25% per surface might be expected. The lack of broadband features also would mean that the compromise coating centered at 710 nm and used for the two inner surfaces of a KDP array would reflect even more at the harmonic wavelengths. This disadvantage would be outweighed by the advantage of a one-coat system and the extreme ease of application.

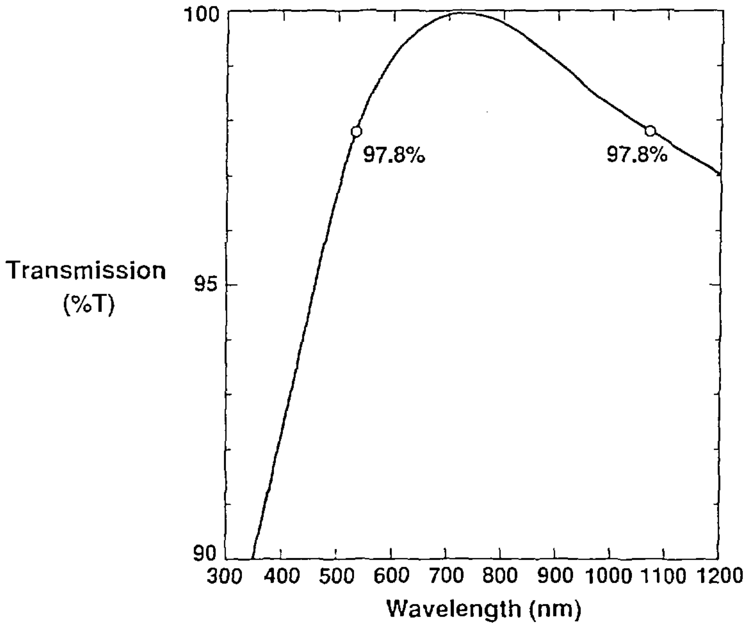

Fig. 5. Theoretical transmission of compromise coating for 1064 nm and 532 nm.

5. EXPERIMENTAL

5.1. 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.

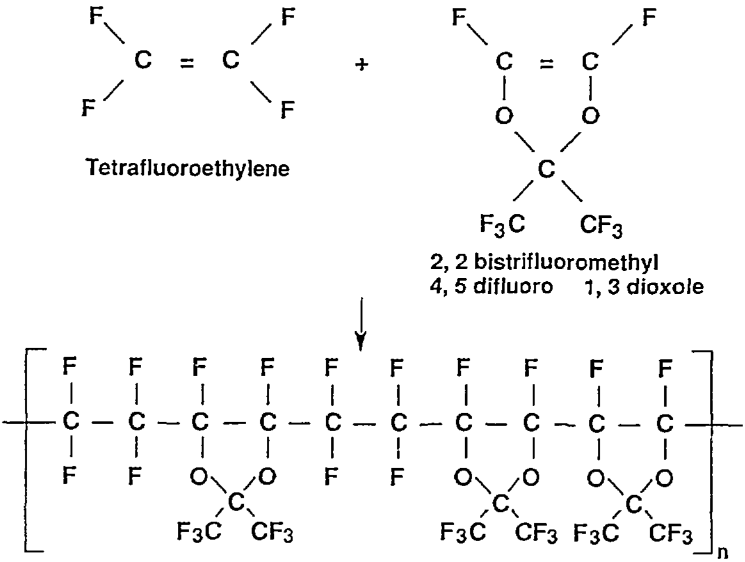

Fig. 6. Polymerization and structure of Teflon® AF 2400.

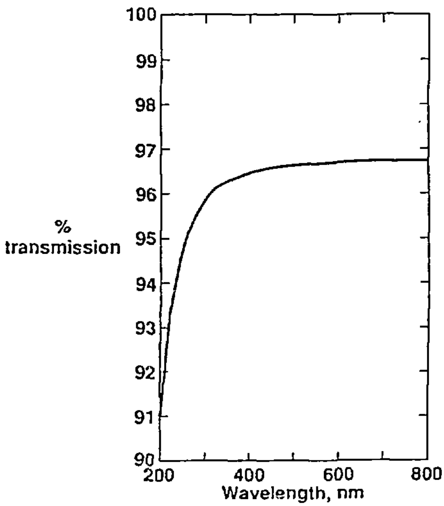

Fig. 7. Transmission of a 1 mil. free-film of Teflon® AF 2400.

5.2. 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.

5.3. Teflon® AF 2400

A 1.25% solution of DuPont Teflon® AF 2400 in Fluorinert® FC-75 was prepared by stirring the powdered polymer in the solvent at room temperature. Fluorinert® FC-75 is perfluorinated ether b.p. 105° manufactured by the 3M Company. Because of the high molecular weight of the polymer complete dissolution took about 24 hours. The solution was filtered through a 1 µm glass fiber filter after preparation.

5.4. 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.

5.5. Coating procedure

Samples were either dip or spun 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).

Teflon® AF 2400 coatings were deposited by dip or spin and the thicknesses adjusted as necessary for the relevant wavelength by variation in withdrawal rate or spin speed.

5.6. Damage threshold measurements

The damage thresholds of all samples were measured on our Nd:YAG Reptile facility(4) 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.

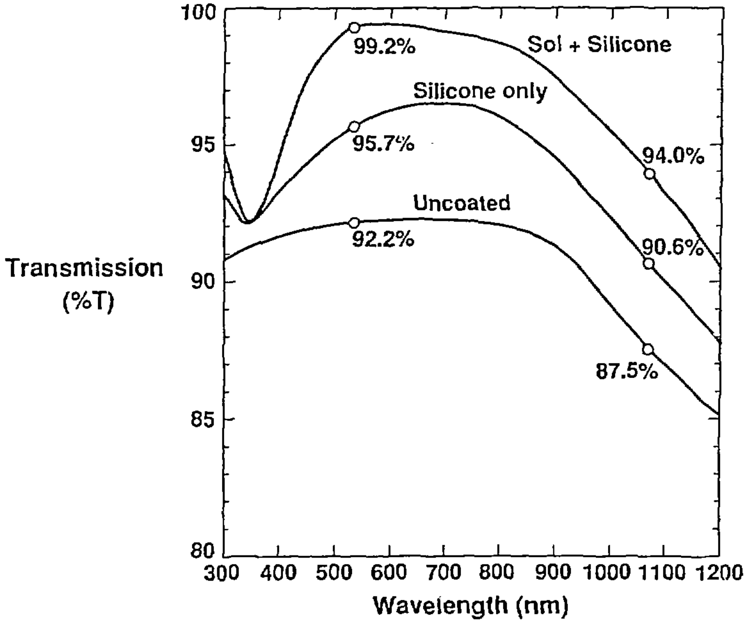

Fig. 8. Transmission curves for KDP coated for 532 nm and 1064 nm.

6. DISCUSSION OF RESULTS

6.1. 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. 8. 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 thus gives a 7.0% and 6.5% increase in transmission two surfaces at the two wavelengths of interest. This is close to what we expected from the theoretical calculations described earlier.

The corresponding transmission curve for the KDP surface to be used at 355 nm is shown in Fig. 9. 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.

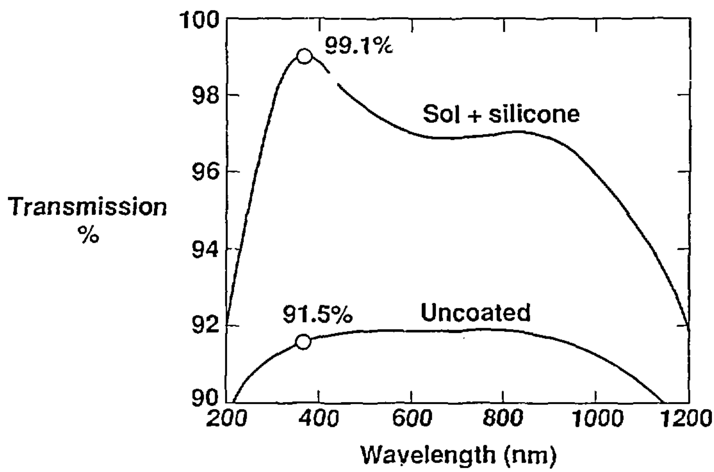

Fig. 9. Transmission curve for KDP coated for 355 nm.

The transmission curve for a KDP crystal coated with Teflon® AF 2400 for use at 1064 nm is shown in Fig. 10. This is a classic single layer quarterwave coating with the minimum (halfwave point) at 532 nm and another maximum at 355 nm. As the index of the coating is 1.29 the efficiency is a little reduced and a two surface improvement of 6.0% is obtained at 1064 nm. Obviously this coating could be used for the 355 nm surface or alternatively one of one-third the thickness. For the two wavelength surfaces where a compromise coating maximized at 710 nm is required, the transmissions at both 532 nm and 1064 nm would be reduced another 1% per surface.

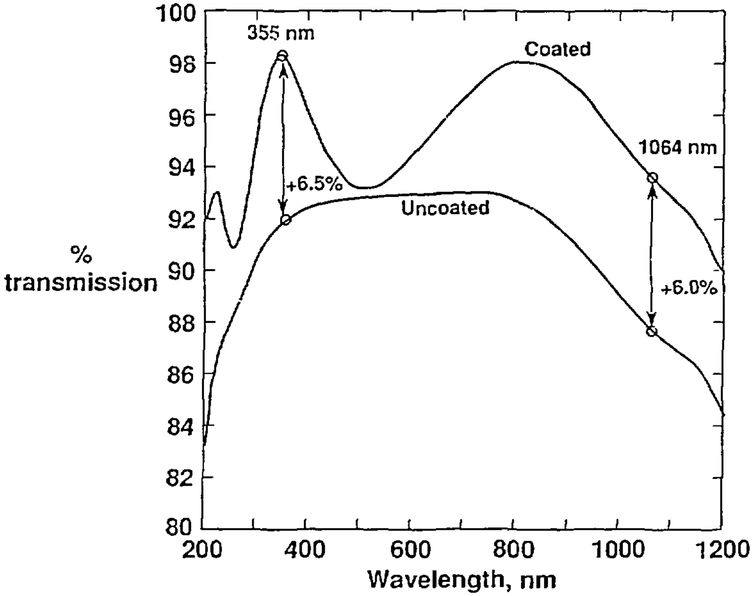

Fig. 10. Transmission curve for KDP coated with Teflon® AF 2400.

6.2. Damage thresholds

The damage thresholds of both types of coating, with KDP bare surface levels for comparison, are shown in Table 1. All levels reported are for conditioned samples although we found that there was little difference between conditioned and unconditioned values for the two coating systems. With bare surface KDP, however, conditioned values are always higher. Damage was in all cases minor at the reported fluences and did not became massive until exposed to considerably higher levels.

At 1064 nm both coating thresholds are comparable to the bare KDP. We have not quoted exact values because bulk damage becomes significant at these levels and it is sometimes difficult to make measurements. A level of 40 J/cm^2 is quite adequate for any laser system currently under design at LLNL. At 355 nm the bare KDP is definitely superior to the coating samples through again all values are quite adequate if one assumes a conversion efficiency of 50-60% for the KDP.

Table 1. Damage threshold levels of coated and bare surface KDP.

Coating	1064 nm / 10 ns	355 nm / 10 ns
Silicone-sol	> 40 J/cm^2	20 J/cm^2
Teflon® AF 2400	> 40	17
Bare surface KDP	> 40	20-30

7 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 the Teflon® AF 2400 is only 206 nm for use at 1064 nm and 69 nm for the 355 nm surface. These thicknesses are 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 coatings 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-silcone system, used on the Nova, which was described earlier. This gave a considerable reduction in the rate of loss of transmission over the long term. Our current tests with the coating of the whole Nova array should confirm this.

8. SUMMARY

We have evaluated two coating systems which can give environmental protection to KDP surfaces as well as optical improvement.

The first is a two layer system incorporating a dense methyl silicone base coat with a porous silica overcoat. The thicknesses of the layers can be arranged to give very low reflections at 1064 nm, 532 nm and 355 nm. The environmental protection given to the crystal surface, which is solely due to the methyl silicone layer, results in a fogging rate which is about three times less than that of an unprotected surface.

The second system was a single layer process in which the KDP crystal was coated with a dense perfluorinated polymer, Teflon® AF 2400. Not only did this dense coating give environmental protection but its extremely low refractive index gave excellent AR properties as well. The extreme ease of application made up for a slightly inferior optical performance when compared to the sol-silicone system.

The laser damage thresholds of both coatings was more than adequate for use in harmonic converter arrays in any current high power laser system.

9. REFERENCES

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