COO-4029-3

EXPLORATORY DEVELOPMENT OF FUSION CAST CALCIUM FLUORIDE FOR 1.06 MICROMETER PULSED LASER OPTICS

Progress Report
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ABSTRACT

This program is an assessment of fusion cast polycrystalline calcium fluoride for optical components of 1.064 micrometer pulsed laser fusion systems. Task areas include casting of essentially stress-free 33 centimeter diameter, 5 centimeter thick ingots, developing surface finishing techniques for optically figured plane and spherical surfaces, and evaluating state-of-the-art antireflection coatings deposited onto specimens of the cast material.

During the third quarter, three casting runs were completed in the large casting furnace, none of which was wholly successful. A decision to limit the remainder of the casting effort to six-inch (15-centimeter) diameter pieces was made. Two chemically homogeneous castings of CaF_2/Nd were made in a second furnace.

Diamond abrasive polishing techniques were used successfully to fabricate a 15-centimeter radius convex spherical surface on one polycrystalline casting and a quarter wave plane surface on a second. Both surfaces were free of grain boundary relief which is commonly produced by standard techniques.

Antireflection coatings obtained from two vendors were found to be physically durable and optically uniform. The components of these coatings are those also used by the vendors for their laser damage resistant coatings on glass, so it is reasonable to anticipate that they will be damage resistant on the fluoride as well. Damage testing will be carried out during the final quarter of the program.

This report has been assigned Raytheon internal number S-2216.

1.0 INTRODUCTION

This program is an assessment of fusion cast polycrystalline calcium fluoride for optical components of high-power, short-pulse laser systems operating at 1.064 micrometers. Calcium fluoride is an attractive material for such systems because its index of refraction (1.428) and non-linear index (0.57×10^{-13} esu) are lower than for most optical glasses. Figure of merit calculations indicate that calcium fluoride components should have approximately twice the power-handling capacity of those fabricated from the presently-employed BK-7 glass. Fusion cast calcium and strontium fluorides, which have been under development at Raytheon primarily for use in the 3-5 micrometer spectral band, are extremely pure materials and have the lowest reported optical absorptivities at these wavelengths. While the extremely low absorptivity of these materials is not required for the pulsed laser operation, we believe the high purity it indicates will assure that the material will have maximum laser damage thresholds.

The program is broken down into three essentially independent tasks so that a complete assessment of the fusion cast material as an optical component candidate can be made. The primary task is the casting itself. In this task, we seek to determine the casting procedures which will produce ingots free of both growth defects and stress birefringence. During the first three quarters of this program, the elimination of stress birefringence from the ingots has emerged as the primary obstacle to be covercome if the fusion cast material is to be a useful fusion laser material.

The remaining program tasks evaluate operations which are required to fabricate finished optical components from the cast ingots. Optical polishing procedures which have been developed to produced highly perfect surfaces on smaller specimens of these polycrystalline materials will be extended to a 15 centimeter plane piece, a spherical surface on a 15 centimeter piece, and to a plane surface on a full 33 centimeter ingot. Standard procedures produce grain-to-grain relief on the surfaces during the final polishing stages.

Two commercial optical coating vendors will deposit their state-of-the-art high power laser antireflection coatings onto specimens of fusion cast calcium fluoride. These will be subjected to the standard environmental and adhesion tests and to laser damage thresholds measurements at Raytheon using 100 nanosecond 1.06 μm pulses and at Lawrence Livermore Laboratories using sub-nanosecond pulses. Surface and bulk damage measurements will be made on uncoated material.

At the conclusion of the program, the assembled results of the tasks should provide an intelligent assessment of the usefulness of large fusion cast fluoride optical components and of their prospective availability.

2.0 PROGRESS

2.1 Fusion Casting

Three casting runs were made in the large casting furnace during the report period. Two 9-centimeter castings of calcium fluoride containing approximately two mole percent neodymiium were made on one of the smaller casting furnaces.

Fabrication of the parts required for modification of a second large furnace for casting was completed, and two preliminary trials were carried out. As discussed in our second quarterly report, this furnace is heated by a long cylindrical heating element. We attempted to produce a vertical gradient in the middile of an otherwise nearly uniform hot zone by means of a cold helium flow piped to the crucible bottom and distributed over it. Our reactive gas and several thermocouples were introduced through separate graphite tubes to the crucible bottom. While the overall design did permit a vertical gradient to be produced in the furnace, the feedthroughs used to bring the gases and thermocouples into the furnace could not withstand the high temperatures required for melting the fluoride. The feedthrough flange must be modified to permit the fittings to be water cooled.

Two neodymium-doped castings were made in response to a request from Dr. M. Weber, Lawrence Livermore Laboratories. These were produced as 9-centimeter ingots in a vacuum furnace which contains a radially-heated volume approximately 20 centimeters diameter and 25 centimeters high. A vertical gradient is produced by water cooling the pedestal on which the crucible is placed. After solidification is complete, the crucible is raised to the middle of the hot zone to minimize the gradient, and the ingot is cooled to room temperature. When used to produce pure alkaline earth fluorides, this fumace produces highly strained, but generally uncracked, ingots up to approximately 11 centimeters diameter. These are then annealed to permit fabrication and evaluation. The two neodymium-doped castings were both cracked when they were removed from the furnace, and the first of the two contained the porosity which is characteristic of too rapid solidification. The cooling rate was decreased for the second casting, and a defect-free, though cracked ingot was produced.

Both ingots had the uniform purple color characteristic of the neodymium ion. The neodymium content was examined by electron microprobe analysis and found to be uniform from the bottom to the top of the ingots and uniform across grain boundaries within them. Microhardness measurements were made using a Kentron microhardness tester (Knoop indenter, 50 gram load). The hardness of the material was 298 ± 11 kg/ mm^2, approximately 50 percent higher than undoped material. Specimens from both ingots were delivered to Dr. Weber for spectrographic analysis.

These castings demonstrate that chemically uniform, rare earth-doped polycrystalline CaF_2 can be produced by fusion casting. Chemical uniformity is largely dictated by the thermodynamics and kinetics of the solidification process, and little could have been done to improve a serious lack of uniformity. The cracking, however, is a more process-dependent phenomenon which should be avoidable with improved process control. We believe that solution of the ingot stress problems for undoped ingots should make doped ingots possible as well. Since the doped material should have a lower thermal conductivity than the undoped, however, it could be more susceptible to thermal shock.

Three castings attempts (runs CF3-9, -10 and -11) were made in the large casting furnace during the report period. The first run was a repeat of an earlier casting (performed on another program) which produced three 15-centimeter (6-inch) diameter ingots which were transparent and free of visible bulk defects. Two of the three ingots were sound; the third was cracked. Maximum stress birefringence in the uncracked ingots was approximately 20 nm/ cm. The remaining two castings made for this program were attempts to produce full-size (33-centimeter) ingots.

For the repeat run with 15-centimeter ingots, the temperature difference between the top and bottom of the crucible during solidification was increased from 85 to 100° C to promote defect-free crystallization. The cooling rate of the solidified ingot was decreased to 4-6° / hour in an attempt to avoid thermal stresses. Ingots and crucible placement within the furnace is shown in Figure 1. The reactive gas is introduced ingot cavity I through a graphite tube from the furnace bottom. The gas flows through cavities II and III and is exhausted from the closed crucible through a second pipe.

Unfortunately, the castings produced in the run were all defective. Ingot I (produced in cavity I) appeared to have crystallized from all directions rather than from bottom to top. It had an average grain size of 1-2 centimeters, finer than most fusion cast material, and the grains did not extent through the thickness of the ingot. Impurities and/ or gas which could not escape were trapped at grain boundaries in ingot. The ingot in cavity II appeared to have crystallized directionally (bottom to top) but at a rate which did not permit defects to be excluded from the growth interface. The third ingot was essentially defect-free but cracked.

While we do not know in details what occurred during the run to produce the defective castings, some comments can be made about the run. First, the reactive gas flow appears to be influencing the crystallization behavior. The crystallization step becomes more "orderly" in the same sequence as the gas flows through the multi-cavity crucible. We believe the gas flow helps stir the molten fluoride and thereby decreases the thermal gradient in it. There may also be a cooling effect, but at the low flow rate we employ (3.3×10^{-3} grams/ sec), it should be quite small. Second, the vertical temperature gradient inside the crucible must be substantially lower than our measurements outside the crucible indicate it to be. The gas flow should not be able to negate a 100° C temperature difference across the growing ingot. Finally, the existing conditions, though unacceptable, must be reasonably close to those which produce defect-free castings; the run conditions of an earlier, more successful casting were essentially repeated for this one.

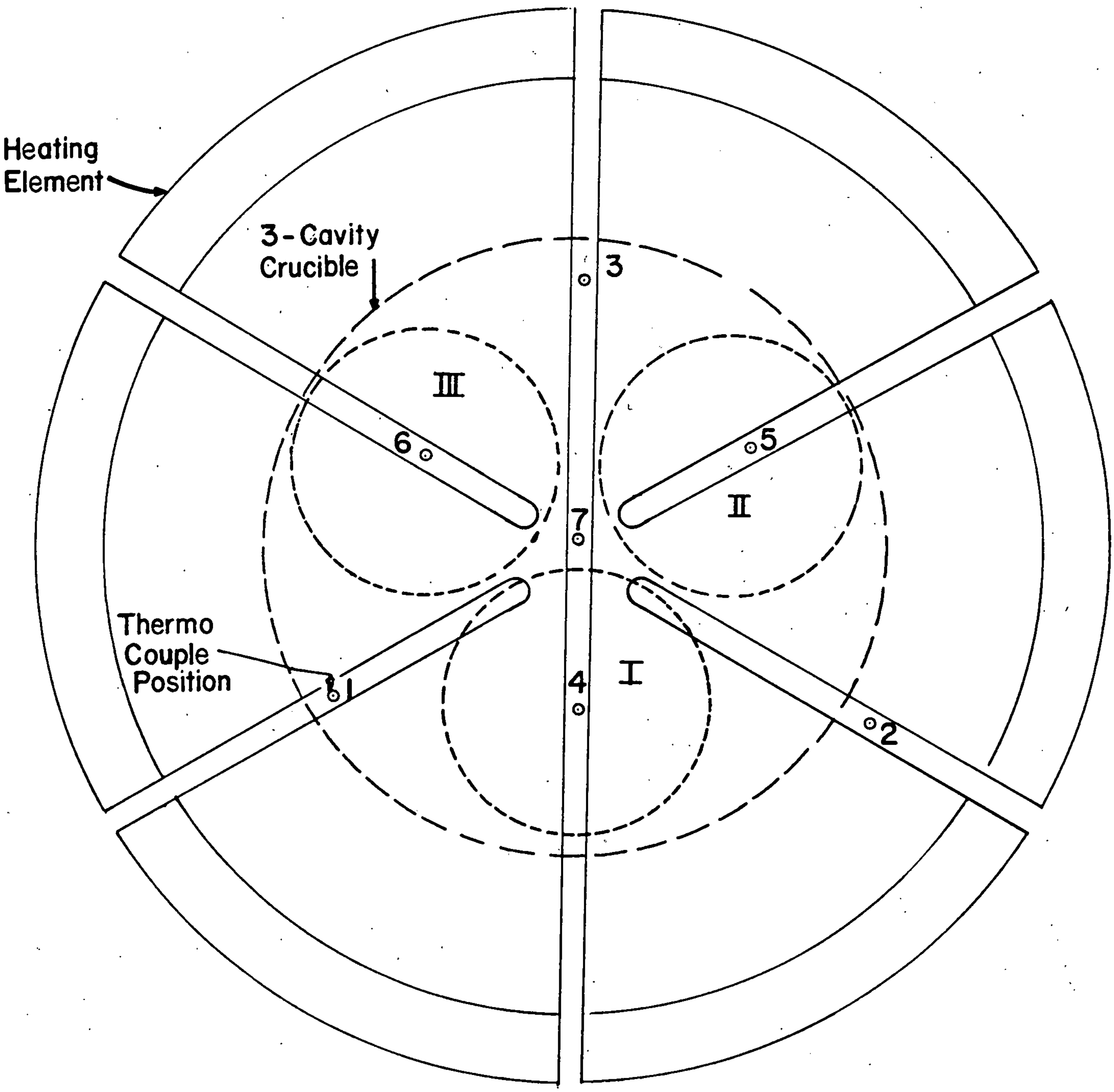

Figure 1. Crucible Placement for 15-centimeter Ingots.

The two crack-free ingots from this run were used for the fabrication effort discussed in paragraph 2.2.

Of the two full-size casting attempts made, only one (CF3-11) actually produced an ingot. Run CF3-10 was in fact a succession of casting attempts which were terminated by failures of the platinum thermocouples. The difficulty was found to be a silicon impurity in our new, ostensibly highly purified graphite crucible. The silicon was removed by heating the crucible to 1600° C in a chlorine atmosphere. The final run of the quarter was made in the purified full-size crucible. This was the first casting made in a large crucible which was also closed to contain the reactive atmosphere. For this run, the incoming gas was deflected to the underside of the crucible lid by a section of graphite tube. Run conditions were similar to those used previously.

A microstructure trace of ingot CF3-11 is given in Figure 2. The ingot was cracked and contained inclusions in the upper half of its thickness produced by too rapid crystallization. In addition, a point of impingement of the gas flow could be seen on the top surface of the ingot just above a region of maximum stress within the ingot. The gas stream did not diffuse after deflecting from the crucible top before it struck the melt surface.

In addition to the gas flow difficulties, the thermal design of the large casting furnace remains unsatisfactory. Both in-house and manufacturer-initiated redesign efforts have appeared unsatisfactory. The present state of the furnace can be seen in the temperature readings in Table 1, taken during the "annealing" portion of run CF3-11, when stresses occurring during the solidification were to be annealed. The furnace contains seven thermocouples above and seven below the crucible. Thermocouple beads are located in recesses in the crucible top and bottom. Each set includes a center thermocouple, three at 7.5 centimeters radius, and three at 15 centimeters radius. Positions are shown as numbers in Figure 1.

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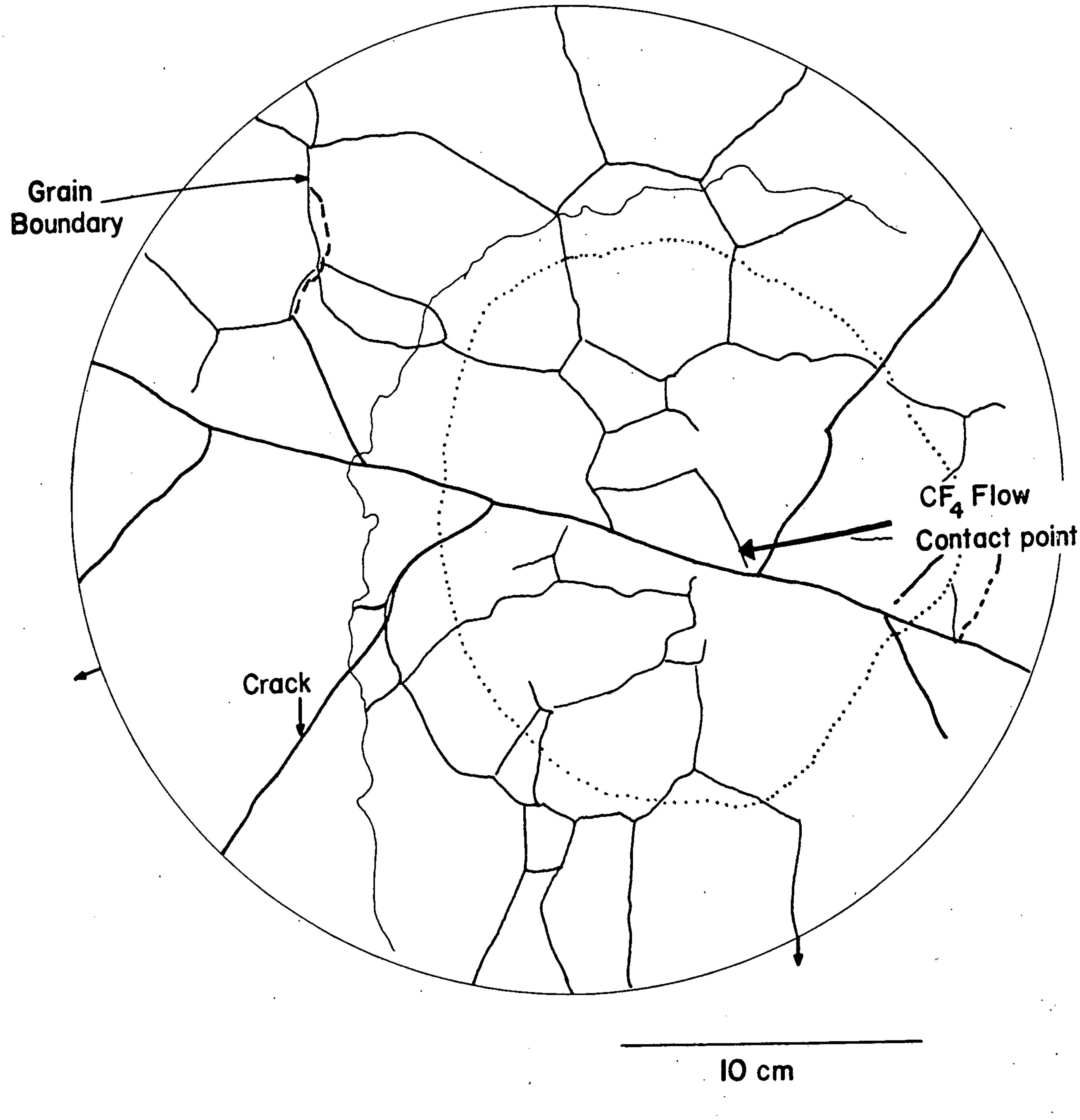

Figure 2. Microstructure of Ingot CF3-11.

TABLE 1

LARGE CASTING FURNACE TEMPERATURE UNIFORMITY

	15 cm radius			7.5 cm radius			center
Thermocouple Number	1	2	3	4	5	6	7
Top Temperature (° C)	1349	1345	1356	1360	1356	1337	1367
Bottom Temp (° C)	1337	1334	1344	1348	1356	1356	1352

Temperatures at position 5 were matched by the controllers. The approximately 20° C from center to the outer radius of the ingot is the present state of our equipment, and this is already too large to produce acceptable castings. We believe that the remainder of the program would be best served by restricting the size of the ingots to six inches (15 cm) diameter in an attempt to make best use of the furnace as it stands. It appears that a major revision of the equipment would be necessary to substantially improve it and the time lost by the revision would be unacceptable. We view this problem as most unfortunate because, as we show in the following two paragraphs, the fabrication and coating of the polycrystalline material both appear to be quite acceptable.

2.2 Optical Fabrication

The object of this task is to fabricate optically-figured plane and spherical surfaces on polycrystalline fusion cast ingots. Standard optical fabrication techniques frequently produce steps in the surface at grain boundaries because the gentle polishing conditions associated with the final polish remove material from the variously-oriented grains of the material at different rates. In earlier work, we have shown that, for specimens as large as 10 centimeters, a diamond abrasive polishing technique could produce optically-figured low scatter surfaces without grain relief.

The polishing technique can be summarized as follows:

1. Grinding - Carried out using Microgrit Alumina abrasives. Coarse grinding done on cast iron laps. Fine grinding (12 and 5 micrometer abrasives) uses glass laps. Water used to carry the slurry.

2. Polishing - Carried out on pitch laps using loose diamond abrasive.* Water used to carry the slurry. Diamond abrasives of 3 and 1 micrometer sizes produce coarse and fine polishes. A half-micrometer diamond will produce a super polish.

The polishing step is best carried out using the hardest pitch which will not cause scratching of the workpiece. We use Swedish #73 pitch. The slurry is applied to the lap by hand using a brush in the usual optical shop fashion, but once the lap is charged, further liquid additions are the water from the top of the slurry (which contains very little abrasive material). Unlike alumina abrasive polishing, the approach appears to produce an abrasive-charged lap which cuts material from all crystal orientations at the same rate. As polishing proceeds, the abrasives are apparently pressed further into the lap to produce, in effect, a finer abrasive surface. Laps can be resurfaced for finer abrasives by softening them with a torch and repressing them. Occasionally new batches of diamond abrasive powders will contain agglomerates of abrasive particles which will scratch rather than polish surfaces. These may usually be broken up in a small agate mortar.

For this task, two six-inch (15 cm) diameter pieces were finished, one with a plano surface, the other with a convex 15 centimeter radius spherical surface. The two intact ingots from run CF3-9 were used as specimens. The ingot with the smaller grain size (CF3-9-1) was used for the spherical surface because we had not previously used diamond abrasives on spherical surfaces. The smaller grain size increased the probability that grain relief would be

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*From Engis Corporation, 8035 N. Austin Ave., Morton Grove, Ill. 60053.

produced if the technique were only marginally useful. Figure 3 is a photograph of the ground 15-centimeter convex radius of the ingot. The grain boundary positions are indicated in pencil. The piece was polished to approximately one wave (λ = 4358 Å) over the 11-centimeter reference sphere without cuasing relief polishing. The corrections which produced the final figure on the piece would have produced relief polishing had alumina abrasives (e.g., Linde A) been used.

Figure 4 is an interferogram of the figured surface of the 15-centimeter diameter plano surface. The grain size of this ingot is 3-4 centimeters. The surface irregularity is approximately one-half fringe ($\lambda / 4$), and again, no grain boundary relief is apparent. The figure of the spherical surface did not photograph well; the specimen will be submitted, along with its test plate, at the conclusion of the program. Neither of the surfaces were carried to an exacting figure; they were rather polished to an extent that would reveal any difficulties produced by their polycrystalline microstructure.

2.3 Antireflection Coatings

A total of forty (40) one-inch diameter specimens of fusion cast CaF_2 were coated on one side with AR coatings designed for minimum reflectivity at 1.06 μm. Two vendors* made two depositions each onto sets of ten (10) substrates. The substrates were cut from a larger ingot and as many as possible contained two to four grains. The coatings are to be tested for adhesion and abrasion resistance, for uniformity of reflectivity, and eventually for laser breakdown thresholds.

The films from both suppliers were composed of the same materials they have used for their high power laser damage-resistant coatings. Both suppliers use metal oxide films. As shown in Figures 5 and 6, the OCLI design has a broader minimum reflectivity band than the Spectra Physics design. None

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*Spectra Physics, Inc., Mountain View, California, and Optical Coating Laboratories, Santa Rosa, California 95401.

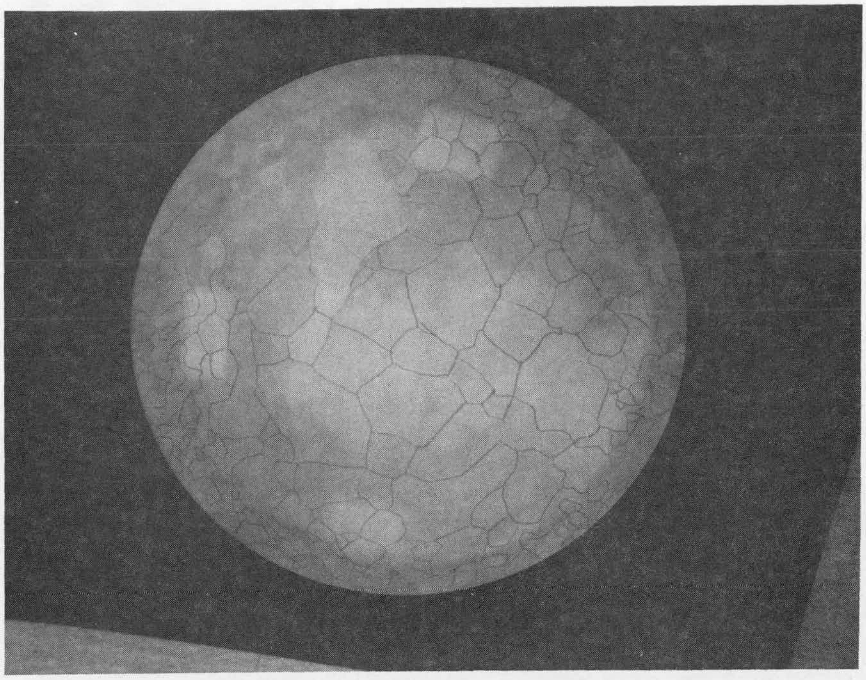


Figure 3 Microstructure of Convex Surface of 15-cm Ingot.

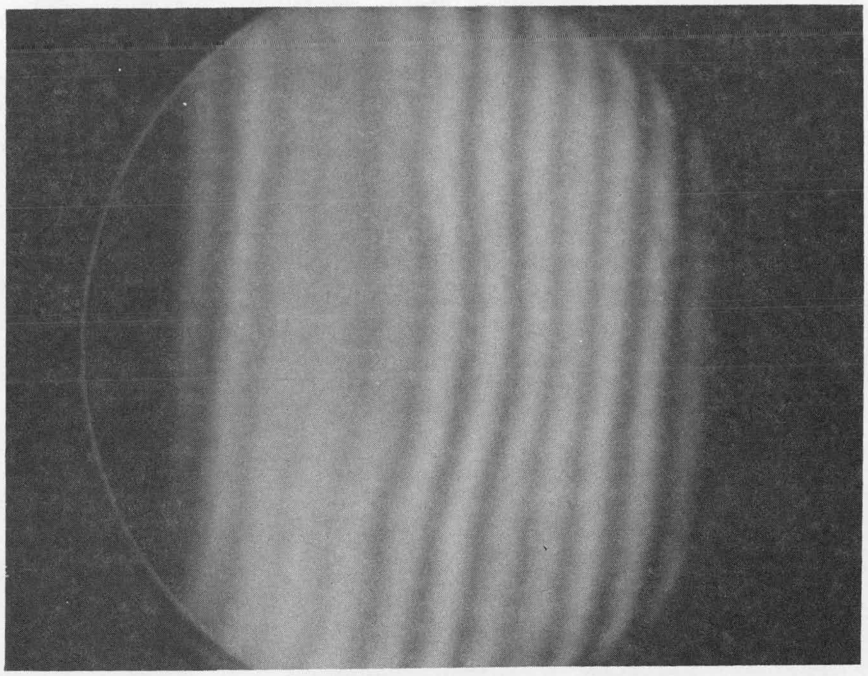
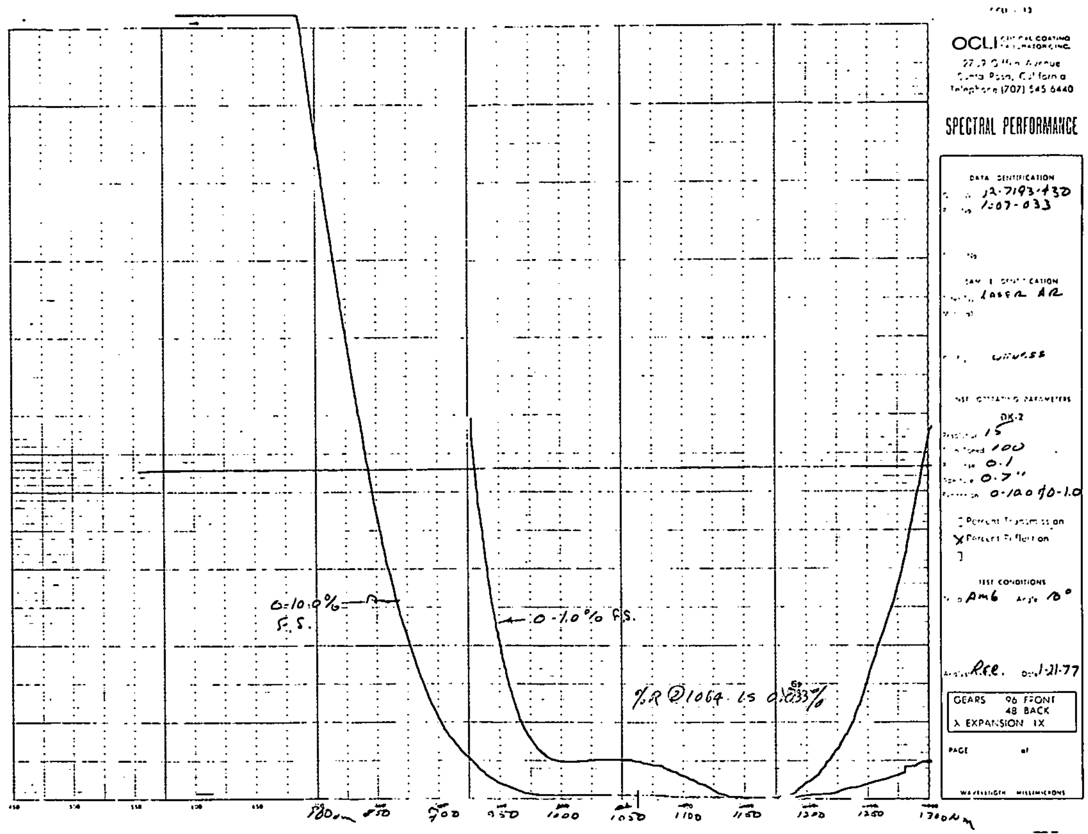
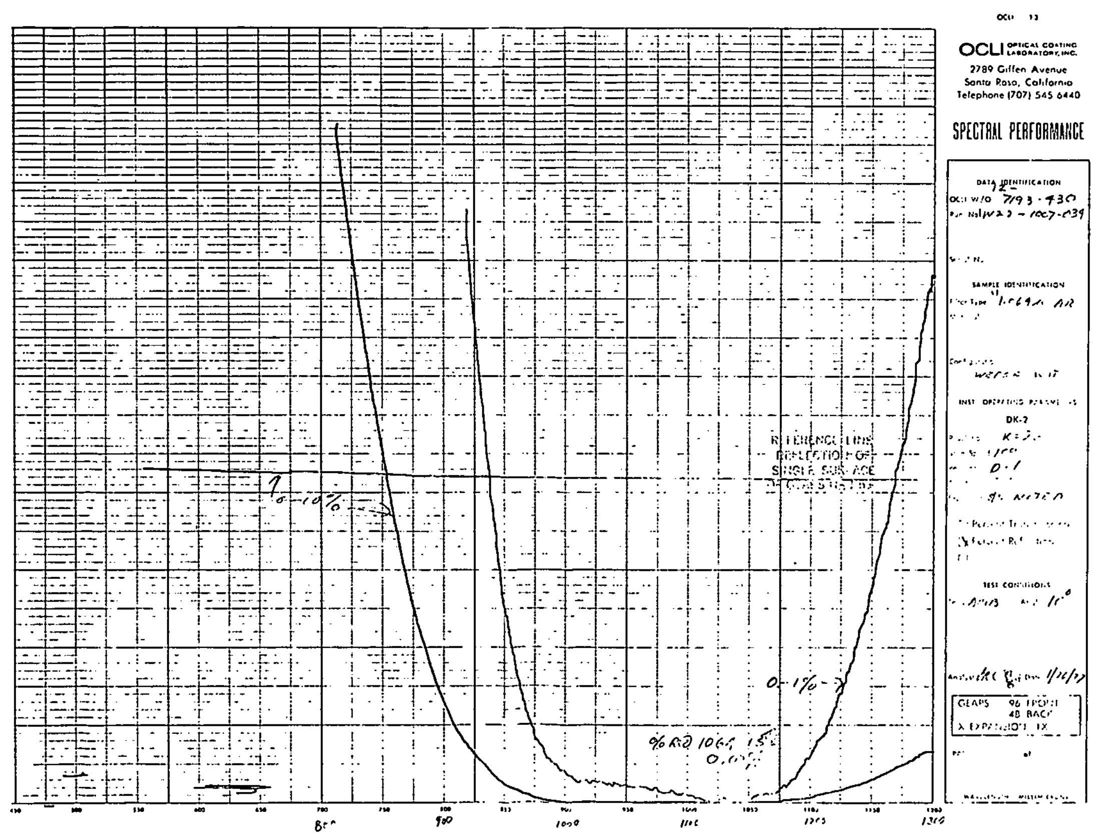


Figure 4 Interferogram of 15-cm CaF_2 Specimen, Plane Surface.

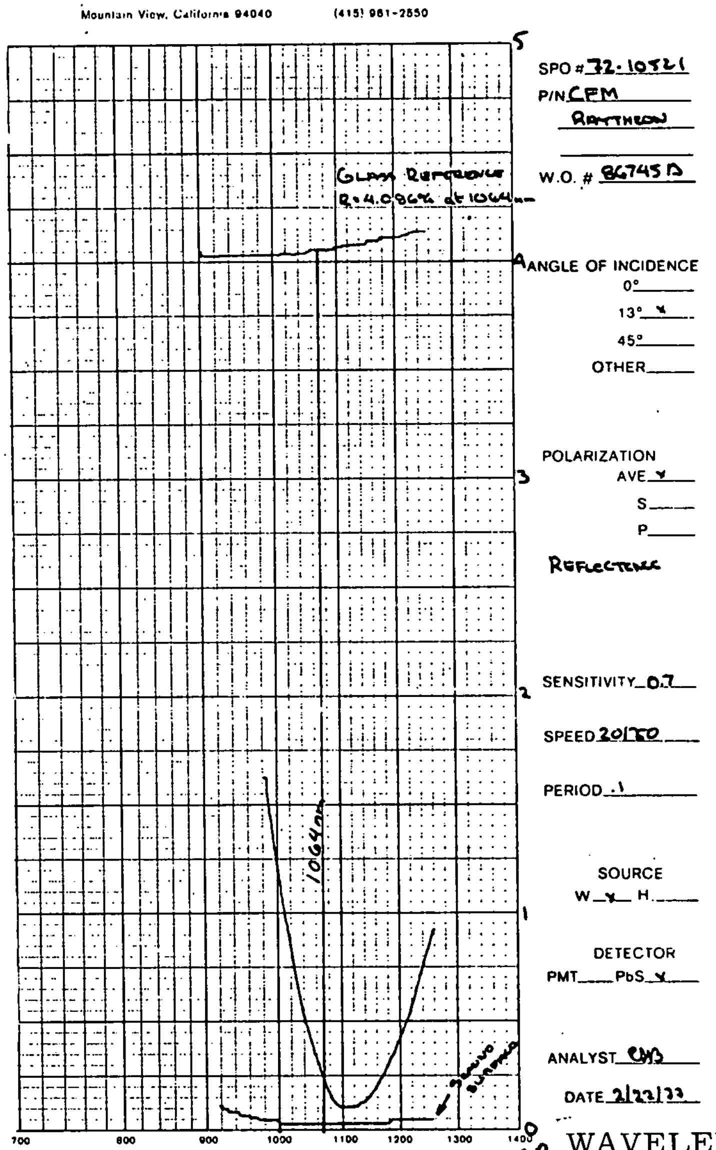


Run No. 1



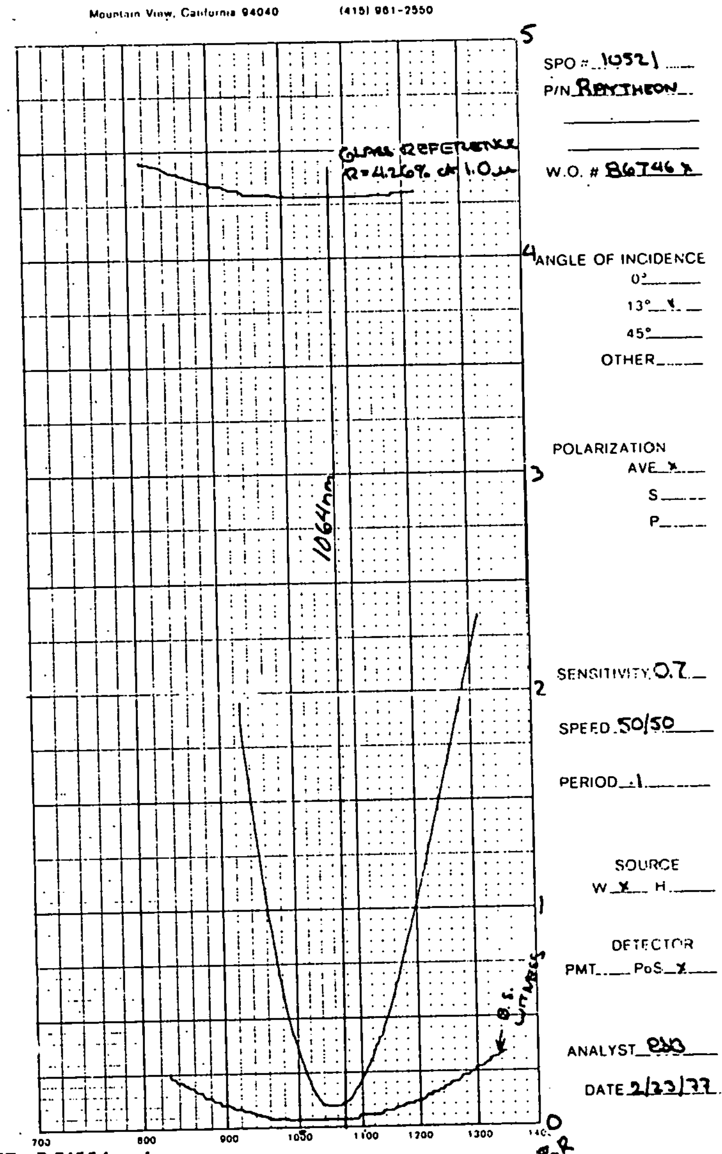
Run No. 2

Figure 5. Reflectance Spectrum of OCLI Antireflection Coatings



Run No. 1

WAVELENGTH-Millimicrons



Run No. 2

Figure 6. Reflectance Spectrum of Spectra Physics Antireflection Coatings

of the four attempts had the minimum reflectivity at exactly the design wavelengths, but the reflectivities of both OCLI depositions were below the target value of 0.1%, and the Spectra Physics coatings were only slightly higher.

The small difference in minimum reflectivity of the two Spectra Physics depositions produces a difference in the visible color of the films. Films from their deposition A are pink in reflection; films from deposition X are gold. Both OCLI depositions have a magenta color.

The uniformity of reflectivity over the polycrystalline substrates was considered to be a potential problem because early investigations of AR coatings for calcium fluoride to be used for 3-5 micrometer lasers had demonstrated that such film materials as lead fluoride and thorium tetrafluoride grew to some extent epitaxially at rates which depended on the substrate orientation. The minimum in reflectivity could then depend upon substrate orientation and therefore on position on polycrystalline materials.

Position dependence of relfectivity on the coated fusion cast specimens was examined in a Beckman Acta MV 4 spectrometer equipped for specular reflectance measurements. Specimens containing two single crystal regions were chosen from each coating run and reflectance spectra were taken from each single crystal region. No position-dependent variation in reflectivity could be detected. Of the forty (40) coated specimens, only one showed any indication of the grain structure of the substrate. Reflectance spectra taken from the two regions are shown in Figure 7. The absolute values of reflectivity have no importance; the two curves are offset from each other. Only the wavelength dependence is significant, and it is the same for both regions. The visual appearance is probably produced by a slight difference in substrate roughness in the two regions.

Castings from all depositions passed the standard* "rubber eraser"

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*MIL - C - 675 -A

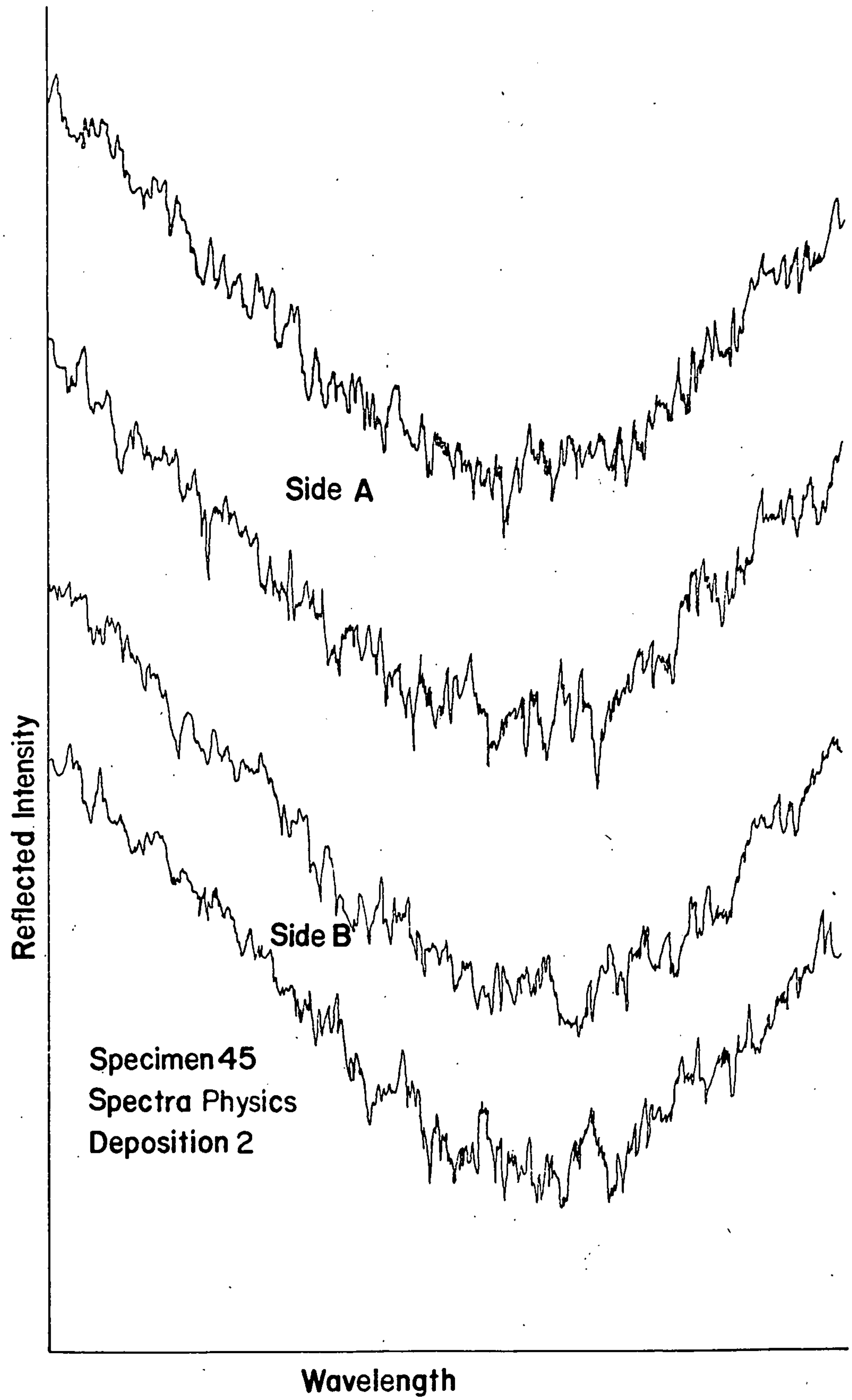

Figure 7. Reflectance Spectra of Spectra Physics AR Coating Over Adjacent Single Crystal Substrate Regions.

abrasion resistance test and cellophane tape adhesion test. They appear to be very hard and durable.

Summarizing, durable antireflection coatings for polycrystalline fluorides composed of materials already in use for laser damage resistant coatings appear to be available. Some "fine tuning" of the design or deposition procedures should make extremely low reflectivity possible. Laser damage testing of the coatings remains to be done.

Specimens of polished and coated materials have been submitted to the Lawrence Livermore Laboratory for evaluation.

3.0 PLANS FOR NEXT QUARTER

During the final quarter of the program, the casting effort will concentrate on the production of six-inch (15-centimeter) diameter ingots in the large casting furnace. This modification of the program thrust should permit the best use of the equipment as it stands.

Laser damage testing of the coated specimens will be carried out.

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