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LOW LOSS WINDOW MATERIALS FOR CHEMICAL  
LASERS

James A. Harrington

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Prepared for:

Army Missile Command  
Defense Advanced Research Projects Agency

July 1974

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Security Classification

AD-784326

## DOCUMENT CONTROL DATA - R &amp; D

Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified

1. ORIGINATING ACTIVITY (Corporate author) The University of Alabama in Huntsville P. O. Box 1247 Huntsville AL 35807		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
3. REPORT TITLE LOW LOSS WINDOW MATERIALS FOR CHEMICAL LASERS		2b. GROUP	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Semi-Annual Technical Report (9 Jan - 9 July 1974)			
5. AUTHOR(S) (First name, middle initial, last name) Horrington, James A.			
6. REPORT DATE July 1974	7a. TOTAL NO OF PAGES 28	7b. NO OF REFS 7	
8a. CONTRACT OR GRANT NO DAAH01-74-C-0437	9a. ORIGINATOR'S REPORT NUMBER(S) UAH Research Report No. 154		
b. PROJECT NO	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U. S. Army Missile Command Redstone Arsenal AL 35809 Attention: AMSMI-RNM	
13. ABSTRACT <p>The main objective of this research program is to study the optical properties of materials suitable for use as low loss chemical laser windows. In order to investigate various candidate materials, measurements will be made of the optical absorption coefficient at DF (3.8 microns) and HF (2.7 microns) frequencies using chemical laser colorimetry. In conjunction with the absorption measurements, chemical polishing techniques will be developed and applied to some materials to minimize surface absorption.</p> <p>Successful polishes were developed for <math>\text{CaF}_2</math> and <math>\text{BaF}_2</math> but no successful polish was found for <math>\text{SrF}_2</math>. Application of the polishes should not only help reduce surface absorption but also minimize laser induced surface damage from high powered lasers.</p> <p>Chemical laser colorimetry was successfully carried out at HF frequencies on two Polytran alkaline earth fluoride (Horshaw Chemical Co.) samples. The results for the absorption coefficient are compared to those obtained from spectrol emittance and CO laser colorimetry measurements. The higher values of the absorption coefficient obtained by HF laser colorimetry as compared to the values obtained by the other two methods are believed to be due to absorption by water bands on the surface or to OH ions in the crystals. Further measurements are planned on these and other materials at HF and DF frequencies. A list of candidate materials is discussed in the report.</p> <p><math>\text{CO}_2</math> laser colorimetry was used to obtain the absorption coefficient for several KCl samples obtained from Dr. Joel Martin, Oklahoma State University.</p>			

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LOW LOSS WINDOW MATERIALS FOR CHEMICAL LASERS

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Semi-Annual Technical Report  
January 9, 1974 to July 9, 1974

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Sponsored by

Defense Advanced Research Projects Agency  
ARPA Order No. 2614

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## PREFACE

This report describes work on Low Loss Window Materials for Chemical Lasers performed during the period from January 9, 1974 to July 9, 1974 on Contract No. DAAH01-74-C-0437, ARPA Order 2614. Participating in the research were, in addition to the principal investigator James A. Harrington, Don Gregory and James Rowe.

### SUMMARY

The main objective of this research program is to study the optical properties of materials suitable for use as low loss chemical laser windows. In order to investigate various candidate materials, measurements will be made of the optical absorption coefficient at DF (3.8 microns) and HF (2.7 microns) frequencies using chemical laser calorimetry. In conjunction with the absorption measurements, chemical polishing techniques will be developed and applied to some materials to minimize surface absorption.

During the initial stages of the research program, while the small cw chemical laser was being constructed for calorimetric measurements, emphasis was placed on developing chemical polishes for the alkaline earth fluorides. Successful polishes were developed for  $\text{CaF}_2$  and  $\text{BaF}_2$  but no successful polish was found for  $\text{SrF}_2$ . Nomarski micrographs, cf. Figs. 1-7, show the effect of polishing on surface scratches. The elimination of the surface scratches and pits should not only help reduce surface absorption but also minimize laser induced surface damage from high powered lasers.

Chemical laser calorimetry was successfully carried out at HF frequencies on two Polytran alkaline earth fluoride (Harshaw Chemical Co.) samples. The results for the absorption coefficient are compared to those obtained from spectral emittance and CO laser

calorimetry measurements. The higher values of the absorption coefficient obtained by HF laser calorimetry as compared to the values obtained by the other two methods are believed to be due to absorption by water bands on the surface or to OH ions in the crystals. Further measurements are planned on these and other materials at HF and DF frequencies. A list of candidate materials is discussed in the report.

CO<sub>2</sub> laser calorimetry was used to obtain the absorption coefficient for several KCl samples obtained from Dr. Joel Martin, Oklahoma State University. All of these data, which lie in the  $10^{-3} \text{ cm}^{-1}$  range at 10.6 microns, were transmitted to OSU as an aid in their crystal growth program.

## TABLE OF CONTENTS

	<u>Page</u>
Preface . . . . .	i
Summary . . . . .	ii
I. Introduction . . . . .	1
II. Plan of Accomplishment . . . . .	1
III. Chemical Polishing of Alkaline Earth Fluorides . . . . .	2
A. Introduction . . . . .	2
B. Nature of Polish for Alkaline Earth Fluorides . . . . .	3
C. Chemical Polishes . . . . .	4
IV. Chemical Laser Calorimetry . . . . .	15
A. Chemical Laser . . . . .	15
B. Chemical Laser Calorimetry . . . . .	15
V. Materials to be Studied at Chemical Laser Wavelengths . . . . .	17
VI. CO <sub>2</sub> Laser Calorimetry . . . . .	18
VII. Conclusions . . . . .	19
References . . . . .	21
Figure Captions . . . . .	22



## I. INTRODUCTION

The primary goal of the research program is to investigate the optical properties of various dielectric materials suitable for use as low loss windows on chemical lasers. Specifically, this involves calorimetric measurements of the optical absorption coefficient at DF and HF frequencies for a variety of candidate materials. In addition to the absorption coefficient measurements, chemical polishing techniques are to be developed and applied to certain window materials in order to determine the effect of chemical polishing on surface absorption.

Surface conditions are studied using interference (Nomarski) microscopy. Nomarski micrographs are used in developing the chemical polishes for alkaline earth fluorides and for investigation of the surface quality of materials which have been degraded in the course of service as an actual window on a chemical laser. In general, surface micrographs are made of all samples received for optical evaluation.

## II. PLAN OF ACCOMPLISHMENT

The research effort is directed toward providing a facility for the optical evaluation of materials at chemical laser frequencies. In order to accomplish this it was necessary first to construct a small cw chemical laser which would act as a convenient and reliable source of laser radiation for the calorimetric measurements of the optical absorption coefficient  $\beta$ . Originally it was planned to use the small screening chemical laser belonging to the Chemical Laser

Group, Propulsion Directorate, U.S. Army Missile Command, Redstone Arsenal, Alabama. However, this idea was abandoned in favor of a laser to be built at the University. Therefore, during the first five months of the contract period when the small chemical laser was being constructed, emphasis was shifted from absorption coefficient measurements to developing chemical polishes for the alkaline earth fluorides. These polishes, which will later be applied to window materials to determine their effect on surface absorption, are discussed in Section III. Section IV contains an account of the calorimetric measurements obtained to data at chemical laser frequencies.

Throughout the contract period our CO<sub>2</sub> laser calorimetric apparatus has been available for those desiring measurements at 10.6 microns. Dr. Joel Martin, Oklahoma State University, has periodically sent assorted KCl samples for measurement of  $\beta$  at 10.6 microns. These results, which are detailed in Section VI, provide valuable feedback to their crystal growth operation.

### III. CHEMICAL POLISHING OF ALKALINE EARTH FLUORIDES

#### A. Introduction

Chemical polishing of laser window materials, especially alkali halides, has proven to be an effective means of reducing surface absorption.<sup>1</sup> For the alkali halides, true chemical polishes have been developed which leave the surface scratch free and exhibit no etching effects. Materials prepared in this manner exhibit not only a reduced surface absorption but also are more resistant to

laser induced surface damage.<sup>2</sup> Chemical polishing also helps remove abrasive particles left by conventional polishing methods which otherwise would lead to increased absorption and a lowering of the laser damage threshold.

#### B. Nature of Polish for Alkaline Earth Fluorides

In developing chemical polishes for laser window materials, one looks ideally for several characteristics. The polish should act as a true polish, that is, remove surface layers of material without exposing mechanical imperfections. From a practical point of view one would also like a polish which has a relatively short working time (no more than several hours) as well as being easy and safe to apply. For the alkali halides, polishes have been developed with these properties. In the case of the alkaline earth fluorides, which have a more restricted range of solubility, one is faced a priori with a more difficult problem. Because of the non-reactive nature of  $\text{CaF}_2$ ,  $\text{BaF}_2$ , and  $\text{SrF}_2$  it was not possible to develop a totally etch free polish, rather polishes were developed which, while they do remove scratches, must be used carefully in order to avoid etch effects. It is felt, however, that this restriction does not detract from the basic usefulness of the polish. One reason for this is that the mechanically polished surfaces of alkaline earth fluorides can be finished to a much smaller scratch depth. This means that a polish need only remove a small amount of surface layer to eradicate the scratch while at the same time not acting long enough to cause etching. Several

polishes which act in this manner on  $\text{CaF}_2$  and  $\text{BaF}_2$  are described below.

### C. Chemical Polishes

In developing chemical polishes one can start with a literature search. Such a search was performed for the alkaline earth fluorides but yielded no significant information. It seems that, in general, polishes, if they exist, are either only casually mentioned in the open literature or are proprietary and remain in corporate vaults (as seems to be the case for sapphire and other materials of interest to the electronics industry).

A number of solutions were tried for polishing  $\text{CaF}_2$ ,  $\text{BaF}_2$ , and  $\text{SrF}_2$ . Some of the attempted polishes along with brief comments as to their effectiveness are listed in Table 1. Most often the solution would either have no effect or it would etch the sample.

The successful polishes for  $\text{CaF}_2$  and  $\text{BaF}_2$  are listed in Table 2. It was found that best results were obtained for  $\text{CaF}_2$  if the acids were fresh and slightly warm (as warm for example, as would result from the heat liberated on mixing the fresh acid). The times listed will depend on the scratch depth. A Nomarski micrograph (800X) of the surface of  $\text{CaF}_2$  before and after polishing (16 min. total time) with the solution in Table 2 is shown in Figs. 1 and 2. No etching effects are visible. (The black spots are probably fine particles of foreign matter.) A similar series of micrographs for  $\text{BaF}_2$  are shown in Figs. 3-5. In this case the  $\text{BaF}_2$  was left in the solution listed in Table 2 for a total of 19 hours

TABLE 1

CHEMICAL POLISHES ATTEMPTED BUT UNSUCCESSFUL

Crystal	Solution	Ratio	Time	Results
CaF <sub>2</sub>	NH <sub>4</sub> Cl/H <sub>2</sub> O	1:1	55 min.	NE
	NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> /H <sub>2</sub> O	1:1	16 min.	NE
	NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> /H <sub>2</sub> O/CH <sub>3</sub> COOH	1:1:1	5 min.	NE
	NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> /H <sub>2</sub> O/CH <sub>3</sub> COOH/HCl	1:1:1:1	20 min.	Etched
	CH <sub>3</sub> COOH/H <sub>2</sub> O	5:2	5 hrs.	NE
	HF/CH <sub>3</sub> COOH	2:3	30 min.	NE
	H <sub>2</sub> SO <sub>4</sub>	-	15 min.	Etched
	H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O	1:3	15 min.	Etched
	H <sub>2</sub> SO <sub>4</sub> /HCl	1:1	1 hr.	Cloudy
	H <sub>3</sub> PO <sub>4</sub>	-	5 hrs.	NE
	H <sub>3</sub> PO <sub>4</sub> /H <sub>2</sub> O	1:1	30 min.	NE
	H <sub>2</sub> O	-	70 min.	NE
	H <sub>3</sub> PO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub>	3:2	18 hrs.	Limited etch
	H <sub>3</sub> PO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub> /H <sub>2</sub> O	6:2:1	24 hrs.	Cloudy
	NH <sub>4</sub> OH	-	2 days	NE
	NaOH	-	2 days	NE
	Hot H <sub>2</sub> O	-	7 min.	NE
BaF <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> /CH <sub>3</sub> COOH	3:2	1 hr.	NE
	H <sub>2</sub> SO <sub>4</sub> /CH <sub>3</sub> COOH	2:1	40 min.	NE
	H <sub>2</sub> SO <sub>4</sub> /CH <sub>3</sub> COOH	4:1	55 min.	Some etch

TABLE 1 (con't)

Crystal	Solution	Ratio	Time	Results
SrF <sub>2</sub>	HF/HCl	1:1	25 min.	Cloudy
	HF	-	15 min.	Cloudy
	HCl/H <sub>2</sub> SO <sub>4</sub>	1:1	15 min.	Cloudy
	HCl/CH <sub>3</sub> COOH	1:1	15 min.	Cloudy
	CH <sub>3</sub> COOH	-	65 min.	NE
	HF/HCl	5:3	40 min.	NE
	Hot H <sub>2</sub> O	-	7 min.	Cloudy
	Hot NH <sub>4</sub> Cl/H <sub>2</sub> O	1:1	10 min.	Cloudy
	CH <sub>3</sub> COOH/H <sub>2</sub> SO <sub>4</sub>	4:1	40 min.	Cloudy
	HCl/HF	1:1	40 min.	NE
	HCl/HF	3:5	40 min.	NE
	HF	-	70 min.	Cloudy
	HCl/H <sub>2</sub> O	3:2	15 min.	Etched
	CH <sub>3</sub> COOH/HF	1:2	15 min.	NE
	CH <sub>3</sub> COOH/HCl/HF/H <sub>2</sub> O	1:1:2:1	40 min.	NE
	HBF <sub>4</sub>	-	1 hr.	NE
	HBF <sub>4</sub> /H <sub>2</sub> O	2:1	50 min.	NE
	Hot H <sub>2</sub> O	-	7 min.	NE
	Hot NH <sub>4</sub> Cl/H <sub>2</sub> O	1:1	10 min.	NE

NE - No effect

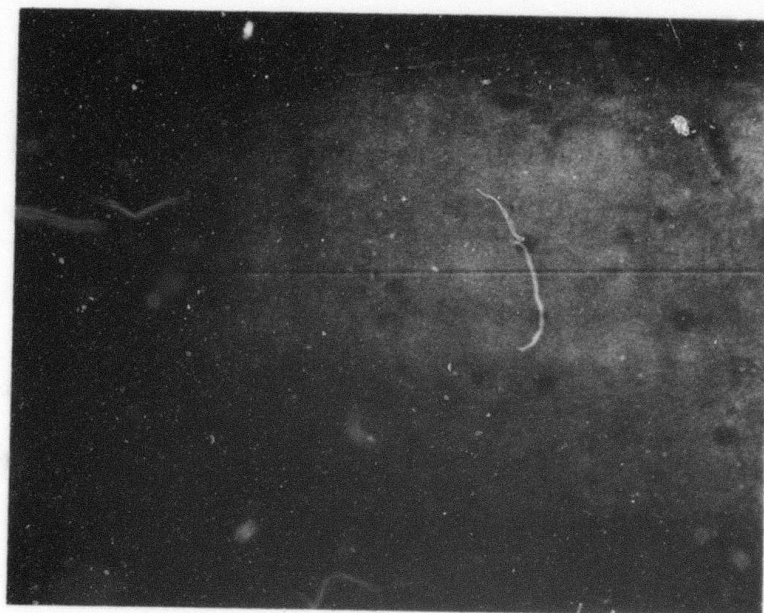


Figure 1

$\text{CaF}_2$ , single crystal, mechanically polished, 800X. Black spots are most likely due to small particles of matter.

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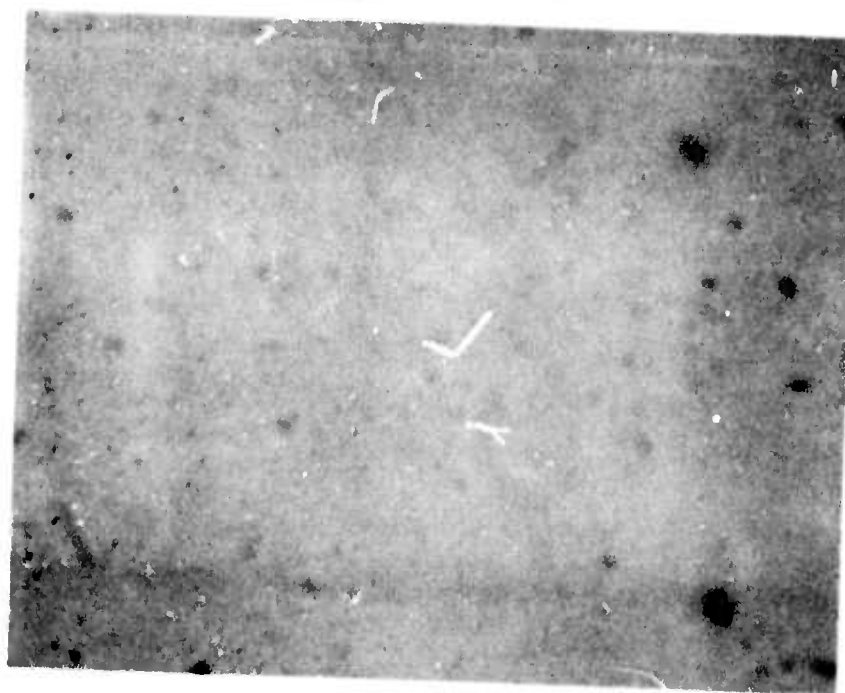


Figure 2

Same  $\text{CaF}_2$  as in Fig. 1 after 16 min. in chemical polish made up of  $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}$  (3:2), 800X. Black spots are most likely due to small particles of matter.





Figure 3

BaF<sub>2</sub>, single crystal, mechanically polished, 280X.

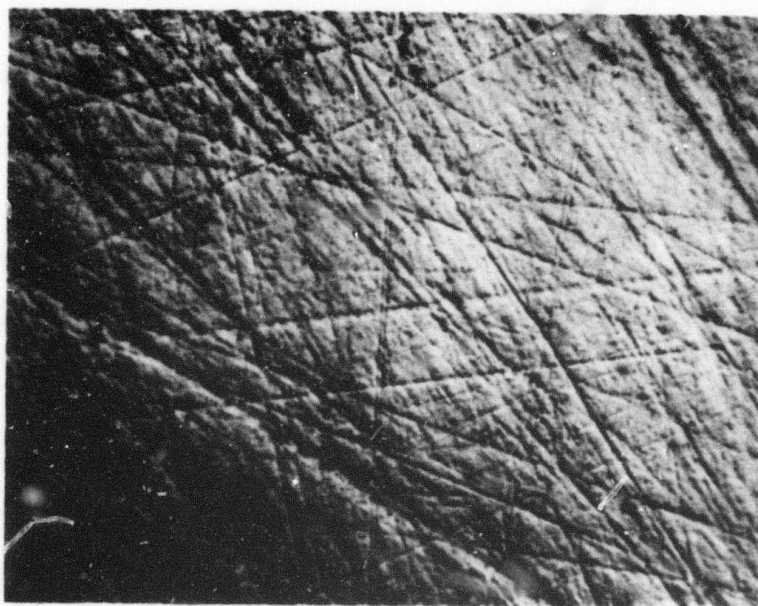


Figure 4

Same  $\text{BaF}_2$  as in Fig. 3, after 6 hours in chemical polish made up of  $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}$  (4:9), 280X. Note fewer scratches remain.

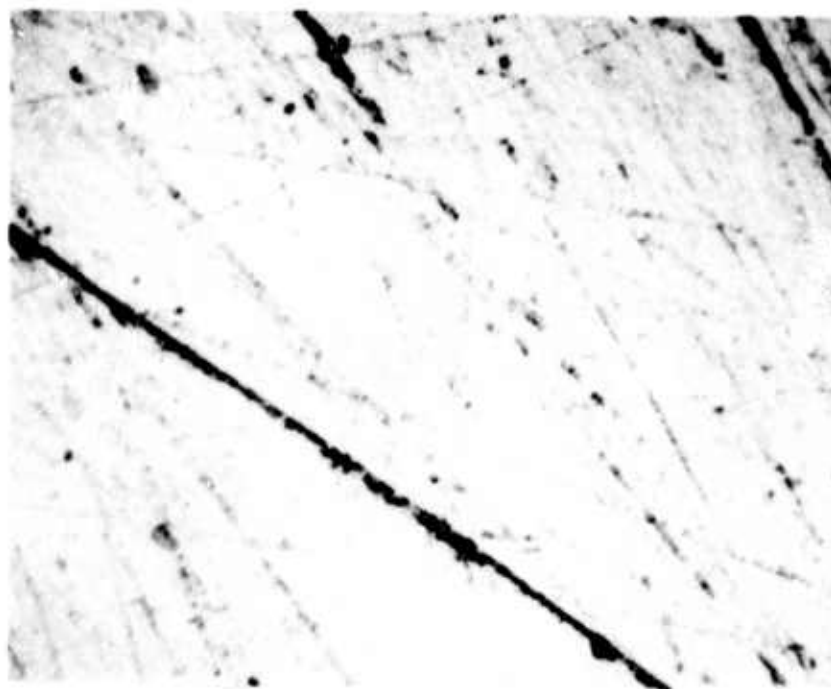


Figure 5

Same  $\text{BaF}_2$  as in Figure 4, after an additional 10 hours in same chemical polish, 280X. Now even fewer scratches remain.

TABLE 2  
SUCCESSFUL CHEMICAL POLISHES FOR  $\text{CaF}_2$  and  $\text{BaF}_2$

Crystal	Solution	Ratio	Time	Comments
$\text{CaF}_2$	$\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}$	3:2	10-16 min. 40 min. is maximum time	Use fresh acids, solution should be warm
$\text{BaF}_2$	$\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}$	4:9	Up to 19 hrs.	No etching observed

and the  $\text{BaF}_2$  was much more deeply scratched than the  $\text{CaF}_2$  yet no pronounced etching effects were observed. Unfortunately, it was not possible to find a good polish for  $\text{SrF}_2$ . The most successful solution was a mixture of  $\text{HCl}/\text{H}_2\text{O}$  (1:3) but etching was detected after 1 1/2 to 2 hours. These negative results are shown in Figs. 6 and 7. This solution, however, might prove useful for shorter times.

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Figure 6

$\text{SrF}_2$ , single crystal, mechanically polished, 280X.



Figure 7

Same  $\text{SrF}_2$  as in Fig. 6, after 1 1/2 hours in chemical solution made up of  $\text{HCl}/\text{H}_2\text{O}$  (1:3). Note severe etching. No suitable polish was developed for this material.

#### IV. CHEMICAL LASER CALORIMETRY

##### A. Chemical Laser

The small cw chemical laser constructed in our laboratory was designed<sup>3</sup> to deliver about 10 watts of multiline power at HF (2.7 microns) frequencies and about 5 watts of multiline power at DF (3.8 microns) frequencies. This power level is quite adequate for calorimetric measurements. At the moment our measurements are being conducted with a multiline power between 1 and 2 watts HF or DF. This power will, however, be increased in the future through the addition of a larger power supply. The laser is stable to within  $\pm 5\%$  and the beam diameter is about 2 x 3 mm.

##### B. Chemical Laser Calorimetry

Calorimetric measurements were performed using a standard air-type calorimeter equipped with differential thermocouples attached to a Keithley nanovoltmeter. The experimental set-up and data analysis follow that of Marvin Hass.<sup>4</sup>

The first samples chosen for measurement were Polytran  $\text{CaF}_2$  and Polytran  $\text{BaF}_2$  kindly provided by Harshaw Chemical Co. Table 3 shows the results of our calorimetric measurements of the absorption coefficient for these two samples at HF frequencies at room temperature. This table also gives, for comparison purposes, results of the absorption coefficient for the same two samples as obtained from CO laser calorimetry and from spectral emittance measurements. The CO (5.25 microns) laser calorimetric results were made by Tom Deutsch of Raytheon and provide an interesting check of our results

TABLE 3  
ABSORPTION COEFFICIENT ( $\text{cm}^{-1}$ ) OF POLYTRAN  $\text{CaF}_2$  AND  $\text{BaF}_2$

Crystal (Polytran Harshaw)	CO Laser Calorimetry 5.25 microns, 293 K T. Deutsch (Raytheon)	Spectral Emittance 5.0 microns, 373 K (NELC)	HF Chemical Laser Calo- rimetry 2.7 microns, 293 K
$\text{CaF}_2$	0.0008	0.0027	0.0025
$\text{BaF}_2$	0.0012	0.0019	0.0044

at 2.7 microns. The important point here is that one would expect, based on the usual extrapolation of frequency versus wavelength curves,<sup>5</sup> that the absorption coefficient in  $\text{CaF}_2$  and  $\text{BaF}_2$  should be extrinsically limited at both 5.25 and 2.7 microns so that  $\beta$  at both wavelengths should be approximately the same. From Table 3 this is obviously not the case (N.B.  $\beta$  in Table 3 represents the total absorption, i.e. no surface absorption has been subtracted out). The discrepancy between the two values is most likely due either to the additional surface absorption at 2.7 microns which would arise from the presence of water bands in this region or to the absorption by  $\text{OH}^-$  present in the crystal. The middle column in Table 3 gives the values of  $\beta$  obtained from spectral emittance measurements performed in cooperation with D. Stierwalt at NELC. It is important to note that these measurements were taken at  $100^\circ \text{C}$  (373 K) and thus



the discrepancy between these values of  $\beta$  and those measured at the CO laser frequency is due in part to the temperature dependence of the absorption coefficient.<sup>6</sup> The higher temperature of the spectral emittance measurements would give a larger absorption coefficient than would be obtained at room temperature. In addition the spectral emittance measurements are hampered by scattered light problems in the region from 5 microns to shorter wavelengths. Further calorimetric measurements are planned on these and other samples at both HF and DF frequencies in order to better understand these discrepancies.

#### V. MATERIALS TO BE STUDIED AT CHEMICAL LASER WAVELENGTHS

The Compendium<sup>7</sup> lists a large number of materials which might be suitable as chemical laser windows. This list, along with the materials and technology already available from CO<sub>2</sub> laser window research, indicates that there should be a variety of substances from which to ultimately select the best window materials. In addition, it is felt that in time the absorption coefficients for the materials listed in the Compendium at 3.0 microns will be improved (lowered) just as was the case for 10.6 micron materials. Therefore one has potentially many materials, with properties very desirable for laser windows, available for chemical laser calorimetry studies.

Some of the materials which are on hand or will be obtained for our measurements are the following: alkali halides, including single and polycrystalline NaCl and KCl and single crystal NaF;

single and polycrystalline alkaline earth fluorides; sapphire, magnesium oxide, Yttralox ceramic, zinc selenide, and strontium titanate. It should be emphasized that this is only a partial list which will be continuously up dated as candidate materials become available. Also, in certain cases such as the alkaline earth fluorides, several sources of supply will be utilized.

#### VI. CO<sub>2</sub> LASER CALORIMETRY

During this reporting period the absorption coefficients of several KCl samples were measured at 10.6 microns using our CO<sub>2</sub> laser calorimeter. The samples were all received from Dr. Joel Martin of Oklahoma State University and were grown under their high purity laser window materials program. The object of the measurements was to provide absorption coefficient data to them to help aid in their crystal growth program.

Table 4 is a list of the KCl samples measured along with the measured  $\beta$ 's and some comments about the samples themselves.

TABLE 4  
ABSORPTION COEFFICIENT MEASUREMENTS AT 10.6 MICRONS  
SAMPLES: OKLAHOMA STATE UNIVERSITY

<u>OSU NO.</u>	<u>SAMPLE</u>	<u><math>\beta</math>(CM<sup>-1</sup>)</u>	<u>COMMENT</u>
112073	KCl	$1.06 \times 10^{-3}$	UTAH MATERIAL
111373	KCl	$3.45 \times 10^{-3}$	RAP TREATED
020565	KCl	$0.92 \times 10^{-3}$	OAK RIDGE
121273	KCl: Sr	$2.84 \times 10^{-3}$	200-500 PPM Sr: RAP
022374	KCl	$1.60 \times 10^{-3}$	RAP TREATED
041874	KCl	$2.0 \times 10^{-3}$	RAP TREATED
042074	KCl	$2.33 \times 10^{-3}$	GROWN IN AR

## VII. CONCLUSIONS

One of the primary goals of the contract has been successfully demonstrated. This is chemical laser calorimetry which has been accomplished using a small cw chemical laser operating at HF and DF frequencies. Using the chemical laser calorimeter, several samples of Polytran alkaline earth fluorides were measured at HF frequencies. The techniques of chemical laser calorimetry will be used to measure a variety of candidate materials at both HF and DF frequencies.

Chemical polishing studies of alkaline earth fluorides, carried out while the chemical laser was being constructed, yielded polishes for  $\text{CaF}_2$  and  $\text{BaF}_2$  but proved more difficult for  $\text{SrF}_2$ . The polishes are seen not to be true polishes in the literal sense for they will etch if left in contact with the window material for too long a time. However, they still serve as useful polishes provided the critical exposure times are not exceeded.

Many materials have yet to be studied at chemical laser frequencies. A list of potentially interesting materials for use in the three micron region is given. It is felt that in time the absorption coefficient in these materials will be reduced through material high purity crystal growth programs. In the meantime samples will continually be measured and the absorption coefficient data fed back to the suppliers as an aid in their growth programs.

#### REFERENCES

1. J. W. Davisson, "Surface Finishing" in Semiannual Report No. 2, ARPA Order No. 2031, U.S. Naval Research Lab., Washington, DC, June, 1973; J. Mat. Sci., to be published.
2. N. Bloembergen, IEEE Journal of Quantum Electronics QE-10, 375 (1974).
3. J. J. Hinchey and C. M. Banas, Appl. Phys. Lett. 17, 386 (1970).
4. M. Hass, in Semiannual Report No. 1, ARPA Order No. 2031, U.S. Naval Research Lab., Washington, DC, Dec., 1972; J. Appl. Phys., to be published.
5. T. Deutsch, J. Phys. Chem. Solids 34, 2091 (1973).
6. J. A. Harrington and M. Hass, Phys. Rev. Lett. 31, 710 (1973).
7. C. S. Sahagian and C. A. Pitha, Compendium on High Power Infrared Laser Window Materials, AFCRL Special Report No. 135, March, 1972.

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#### FIGURE CAPTIONS

- Fig. 1.  $\text{CaF}_2$ , single crystal, mechanically polished, 800X. Black spots are most likely due to small particles of matter.
- Fig. 2. Same  $\text{CaF}_2$  as in Fig. 1, after 16 min. in chemical polish made up of  $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}$  (3:2), 800X. Black spots are most likely due to small particles of matter.
- Fig. 3.  $\text{BaF}_2$ , single crystal, mechanically polished, 280X.
- Fig. 4. Same  $\text{BaF}_2$  as in Fig. 3, after 6 hours in chemical polish made up of  $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}$  (4:9), 280X. Note fewer scratches remain.
- Fig. 5. Same  $\text{BaF}_2$  as in Fig. 4, after an additional 10 hours in same chemical polish, 280X. Now even fewer scratches remain.
- Fig. 6.  $\text{SrF}_2$ , single crystal, mechanically polished, 280X.
- Fig. 7. Same  $\text{SrF}_2$  as in Fig. 6, after 1 1/2 hours in chemical solution made up of  $\text{HCl}/\text{H}_2\text{O}$  (1:3). Note severe etching. No suitable polish was developed for this material.