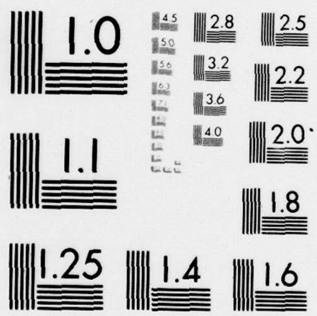
AD-A080 608 ARMY MISSILE COMMAND REDSTONE ARSENAL AL TECHNOLOGY LAB F/G 7/5
ROOM TEMPERATURE SYNTHESIS OF PURE SI, SI3N4, SI3N4ON, AND K2SI--ETC(U)
SEP 79 J A MERRITT, L C WARREN
UNCLASSIFIED DRSMI-T-79-96 NL

| OF |

AD
A080608

END
DATE
FILMED
3-80
DDC


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3

LEVEL II (12) SC

TECHNICAL REPORT T-79-96

ROOM TEMPERATURE SYNTHESIS OF PURE Si, Si_3N_4, $Si_3N_4O_n$, AND K_2SiF_6 BY LASER PHOTOCHEMICAL REACTIONS

J. A. Merritt
L. C. Warren
Research Directorate
Technology Laboratory

21 September 1979

U.S. ARMY MISSILE COMMAND
Redstone Arsenal, Alabama 35809

Approved for public release; distribution unlimited.

DISPOSITION INSTRUCTIONS

DESTROY THIS REPORT WHEN IT IS NO LONGER NEEDED. DO NOT RETURN IT TO THE ORIGINATOR.

DISCLAIMER

THE FINDINGS IN THIS REPORT ARE NOT TO BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION UNLESS SO DESIGNATED BY OTHER AUTHORIZED DOCUMENTS.

TRADE NAMES

USE OF TRADE NAMES OR MANUFACTURERS IN THIS REPORT DOES NOT CONSTITUTE AN OFFICIAL ENDORSEMENT OR APPROVAL OF THE USE OF SUCH COMMERCIAL HARDWARE OR SOFTWARE.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER T-79-96	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Room Temperature Synthesis of Pure Si, Si_3N_4, $Si_3N_4O_n$, and K_2SiF_6 by Laser Photochemical Reactions.		5. TYPE OF REPORT & PERIOD COVERED Technical Report.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J.A. Merritt, L.C. Warren		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Commander, US Army Missile Command, ATTN: DRSMI-RR (R&D), Redstone Arsenal, Alabama 35809		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 24
11. CONTROLLING OFFICE NAME AND ADDRESS Commander, US Army Missile Command, ATTN: DRSMI-TI (R&D), Redstone Arsenal, Alabama 35809		12. REPORT DATE 21 September 1979
		13. NUMBER OF PAGES 22
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) DRSMI-T-79-96		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Silicon Oxynitride
Diffraction Spectrum
Stranmanis Film Technique
Pyrolysis
Beckman 1R5 Spectrometer
Czerny-Turner Monochrometer
Fluorosilicate

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Using 11 watts/cm^2 of 10.764 μm frequency of the P(36) $00^01 - 10^00$ CO_2 laser line as a source to irradiate 35 torr total pressure of the reactants SiH_4 and NF_3 in various ratios of partial pressure at room temperatures, Si_3N_4, pure Si, $Si_3N_4O_n$, K_2SiF_6, and $SiH_{(x)}F_{(y)}$ have been produced. This

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified LB

393 427

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) represents an energy efficiency well over 200 percent and is a cost-effective method of synthesizing the above materials.

CONTENTS

ILLUSTRATIONS

Figure Page

TABLES

Table | Page

I. INTRODUCTION

Pure silicon, silicon nitride, and silicon oxynitride have many attractive properties which are of great interest for microelectronic devices, cladding for fiber optics, etc. Several methods of preparing silicon nitride have been reported in the literature. Commercial silicon nitride particles are produced by heating elemental silicon in either nitrogen[1] or in dehydrated ammonia.[2] Silicon nitride powder also has been prepared by heating silane and dehydrated ammonia.[3]

The production of various compounds by laser excitation has been demonstrated.[4] This method of inducing chemical reactions generally results in products of higher purity than production by conventional thermal (pyrolysis) processes. Thermal processes result from the excitation of the total molecule; both the external (translational) and internal (electronic, vibrational, and rotational) degrees of freedom are usually in thermodynamic equilibrium. The end products often contain impurities that alter the performance of the desired products. These have to be removed, resulting in increased production cost. This problem is greatly reduced in laser photochemical reactions.

This method results in the excitation of a particular bond of the molecule, thus eliminating many undesirable side reactions. In order for this reaction to take place, there must be a frequency correlation between the light source and the reactants. The reaction is carried out by selectively exciting the reactants by applying energy sufficient to excite the molecules above threshold.

The purpose of this research is to investigate the feasibility of making pure silicon and silicon nitride from a mixture of silane and nitrogen trifluoride by exciting a vibrational fundamental of the reactants that is resonant with a frequency of a CO_2 laser. The frequency that best suits these experiments is that of the $P_{(36)}$ 00°1 - 10°0 transition. This line is resonant with a frequency of both the silane and nitrogen trifluoride (929.02 cm^{-1}) (*Figure 1*).

II. EXPERIMENTAL

The silane (semiconductor grade) was obtained from Matheson Gas Products with a minimum purity of 99.95 percent on a hydrogen-free basis.[5] Nitrogen trifluoride (research grade) was obtained from Air Products and Chemicals, Incorporated. There were no additional attempts to further purify either gas. The purity of the gases was sufficient for the intended purpose. (See *Figure 1*).

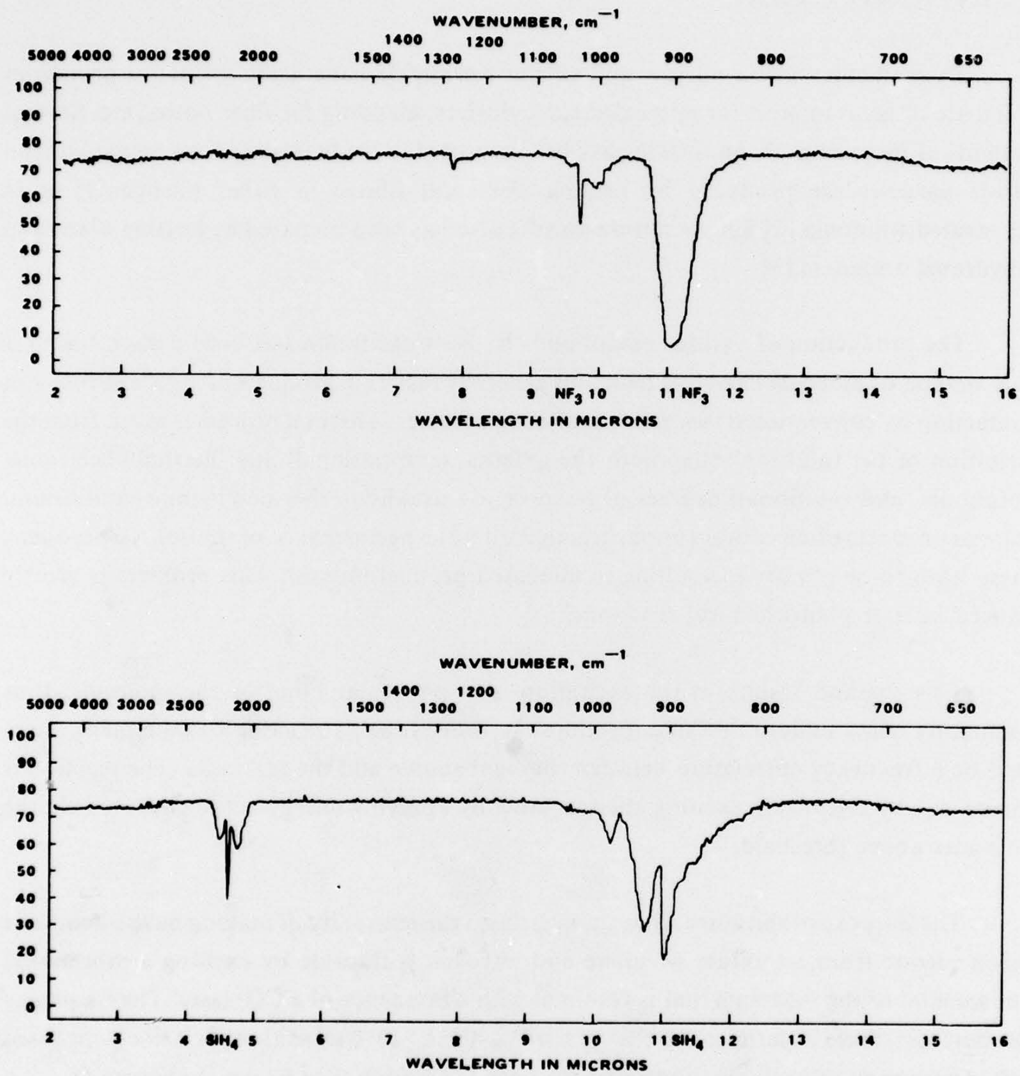


Figure 1. The infrared spectra of the reactants NF_3 and SiH_4 showing the fundamental bands ν_1 of NF_3 and $\nu 4$ of SiH_4 that are resonant with the $P_{(36)}$ 00°1 - 10°0 CO2 laser frequency.

The actual experiments were carried out in brass or stainless steel cells 10 cm in length fitted with two 5 cm diameter KCℓ windows and two glass windows. Irradiation was accomplished with a CW CO_2 grating tunable laser. Spectra were obtained with a Beckman IR5 spectrometer, an x-ray diffractrometer, and a one meter Czerny-Turner monochrometer using photographic detection.

III. DISCUSSION

When a mixture of silane and nitrogen trifluoride was irradiated with 11-15 watts of power at the frequency of the $P_{(36)}$ 00°1 - 10°0 transition of the CW CO_2 laser, solid compounds were formed on the walls and windows of the cell,

$$(xs)\ SiH_4 + NF_3 + nh\nu \longrightarrow Si_{(s)} + N_{2(g)} + SiH_xF_{y(g)} \quad , \tag{1}$$

$$SiH_4 + (xs)\ NF_3 + nh\nu \rightarrow [SiF]^* \longrightarrow Si_3N_4O_{n(s)} + K_2SiF_{6(s)} + SiH_xF_y + Si_3N_{4(s)} \quad . \tag{2}$$

Optical transmittance data of the static gaseous products were obtained over the range from 2 - 16 μ (infrared). The absorption range of the solid Si_3N_4 of Reaction (2) was between 12 - 14 μ with a maximum at 13.6μ. This corresponds to the silicon nitride absorption (between 10 - 14 μ) obtained by pyrolysis, depending on the temperature during production.[6-9] The appearance of the solid is consistent with that of silicon nitride. X-ray diffraction studies of the solid products of Reaction (2) give evidence for a mixture of silicon oxynitride, silicon nitride, and potassium fluorosilicate (*Figures 2* and *3*; *Tables 1, 2, 3*, and *4*), with strong evidence for the latter compound. X-ray diffraction patterns (*Figure 4*, *Tables 5* and *6*) of the solid (Reaction (1)) indicates pure silicon to be the product. The solid of Reaction (1) is brown in color and is consistent with pure silicon produced during rf discharge experiments using pure silane.[9]

Energy of the laser irradiation to initiate the Reactions (1) and (2) is inversely proportional to the total pressure. For a total pressure of about 40 torr, 11 watts/cm^2 will produce a rapid reaction, whereas for a total pressure of about 16 torr, 35 watts/cm^2 is required. All of these total pressures are higher than that required for noncollisional effects.

The reaction products are partial pressure-dependent. If an excess of SiH_4 reactant is used, then Reaction (1) is dominant; if an excess of NF_3 (this reactant has potassium as an impurity) is used, then Reaction (2) results.

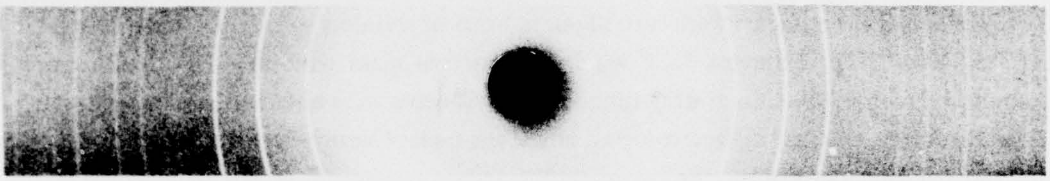


Figure 2. X-ray diffraction spectrum of solid product from Reaction (2). Powder introduced into 0.3 mm capillary. X-ray parameters: 114.6 mm diameter Philips powder camera, no-screen medical x-ray film, Straumanis film technique, CuK α, (Ni filter), 40 kV - 20 MA, 6 hour exposure.

TABLE 1 FIGURE 2—SPECTRUM LINE POSITIONS			TABLE 2 JCPDE CARD NO. 7-127 - $K_2 SiF_6$ (Possible matches only listed)		
LINE	d(Å)	I/I_1	LINE	d(Å)	I/I_1 (estimate)
1	4.707	100	1	4.699	100
2	2.880	60	2	2.877	65
3	2.350	60	3	2.349	71
4	2.038	40	4	2.034	52
5	1.811	1	5	1.819	4
6	1.663	5	6	1.661	12
7	1.568	5	7	1.565	13
8	1.439	7	8	1.438	15
9	1.377	3	9	1.375	5
10	1.287	5	10	1.286	9
11	1.225	2	11	1.226	3
12	1.174	1	12	1.174	2
13	1.144	1			
14	1.089	1	14	1.087	5

IN ORDER FOR THE FOLLOWING TABLES AND FIGURES TO APPEAR TOGETHER, THIS PAGE IS BLANK.

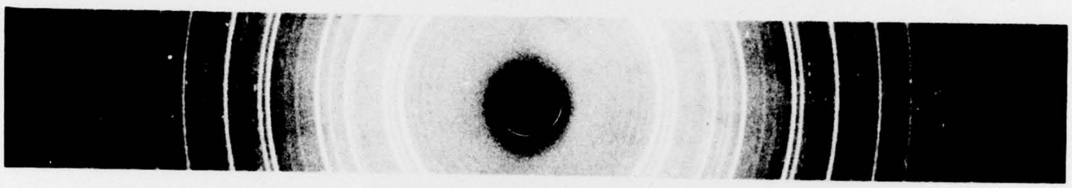


Figure 3. X-ray diffraction spectrum of white solid product from Reaction (2). Powder introduced into 0.3 mm capillary. X-ray parameters: 114.6 mm diameter Philips powder camera, no-screen medical s-ray film, Straumanis film technique, CuKα, (Ni filter), 40 kV - 20 MA, 6 hour exposure.

TABLE 3 FIGURE 3—SPECTRUM LINE POSITIONS			TABLE 4 JCPDE CARD NO. 9-426 - SILICON OXYNITRIDE (possible matches only listed)		
LINE	d(Å)	I/I_1	LINE	d(Å)	I/I_1 (estimate)
1	6.371	VW			
2	5.754	W			
3	5.356	W			
4	5.096	VW			
5	4.733	100	5	4.69	55
6	4.462	40	6	4.44	95
7	4.210	50			
8	3.826	VW			
9	3.453	W			
10	3.320	50	10	3.38	100
11	3.175	W			
12	3.058	10			
13	2.876	50			
14	2.567	VW	14	2.61	40
15	2.529	VW			
16	2.462	VW			
17	2.353	50	17	2.394	40
18	2.287	30	18	2.301	25
19	2.233	VW	19	2.225	3
20	2.106	W	20	2.107	17
21	2.036	40			
22	1.906	W			
23	1.797	10	23	1.797	17
24	1.701	W			
25	1.664	5			
26	1.595	3	26	1.595	25
27	1.567	3			
28	1.542	W			
29	1.481	W			
30	1.455	W			
31	1.439	5			
32	1.398	W			
33	1.375	W	33	1.374	35
34	1.295	3			
35	1.230	W			
36	1.176	VW			
37	1.140	VW			
38	1.088	W			

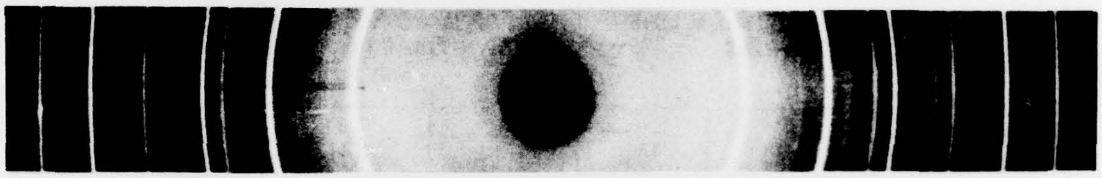


Figure 4. X-ray diffraction spectrum of the brown solid product of Reaction (1). Powder introduced into 0.3 mm capilliary. X-ray parameters: 114.6 mm diameter Philips powder camera, no-screen medical x-ray film, Straumanis film technique, CuKα, (Ni filter), 40 kV - 20 MA, 6 hour exposure.

TABLE 5 FIGURE 4—SPECTRUM LINE POSITIONS			TABLE 6 JCPDE CARD NO. 5-0565 - Si (Possible matches only listed)		
LINE	**d(Å)**	**I/I_1**	**LINE**	**d(Å)**	**I/I_1 (estimate)**
1	3.503	VW			
2	3.411	VW			
3	3.361	VW			
4	3.145	100	4	3.138	100
5	3.061	VW			
6	2.887	VW			
7	2.825	VW			
8	2.745	VW			
9	2.665	VW			
10	2.473	VW			
11	2.231	60			
12	2.112	VW			
13	2.070	VW			
14	1.928	10	14	1.920	60
15	1.855	VW			
16	1.818	25			
17	1.641	5	17	1.638	35
18	1.597	VW			
19	1.573	10			
20	1.409	25			
21	1.287	15			
22	1.247	1	22	1.246	13
23	1.114	4	23	1.1083	17
24	1.049	5	24	1.0450	9
25	0.997	5			
26	0.962	VW	26	0.09599	5
27	0.949	5			
28	0.919	W	28	0.09178	11
29	0.909	VW			
30	0.874	2			
31	0.861	VW	31	0.8586	9
32	0.841	5			
33	0.790	VW	33	0.8281	5

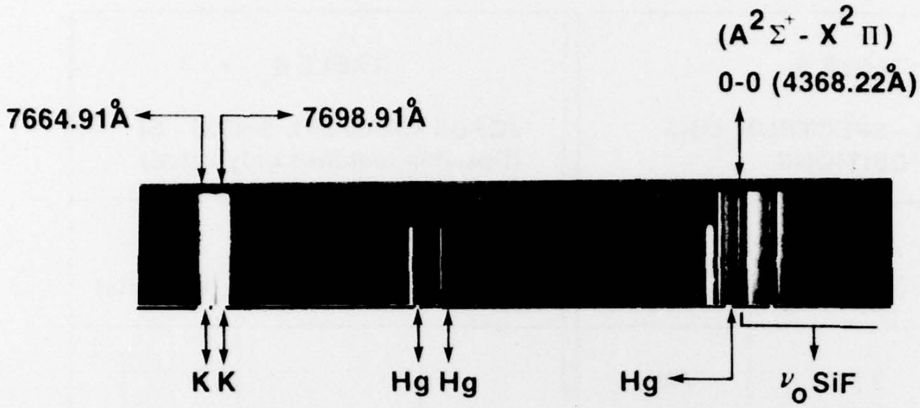


Figure 5. The emission spectrum of SiF intermediate produced by Reactions (1) and (2).

In Reaction (2) the intermediate radical (SiF) (*Figure 5*) is formed in its electronic excited state ($A^2\Sigma^+$) and radiates a strong fluorescence. This spectrum was obtained in a single exposure of millisecond duration on photographic film, indicating its strong intensity. This radical is not observed in Reaction (1).

The solid products Si, $Si_3N_4O_x$, and K_2SiF_6 of the two reactions are identified by x-ray diffraction spectra. The gaseous products SiH_xF_y (where x and y are 0-4) are identified by infrared spectra (*Figure 7*). Also, strong evidence for Si_3N_4 is found from the infrared spectra of *Figure 7* and the x-ray diffraction spectrum (*Figure 6* and *Table 7*). The strong lines of $Si_3N_4O_n$ mixed with the Si_3N_4 mask some of the Si_3N_4 lines in *Figure 6*, but sufficient Si_3N_4 lines can be identified in the spectrum (*Figure 6*) coupled with the evidence of the infrared spectrum (*Figure 7*) to verify that Si_3N_4 is a product of Reaction (2).

IV. RESULTS

Using 11 watts/cm^2 of 10.764 μm frequency of the $P_{(36)}$ 00°1 - 10°0 CO_2 laser line as a source to irradiate 35 torr total pressure of the reactants SiH_4 and NF_3 in various ratios of partial pressure at room temperatures, Si_3N_4, pure Si, $Si_3N_4O_n$, K_2SiF_6, and SiH_xF_y have been produced. This represents an energy efficiency well over 200 percent and is a costeffective method of synthesizing the above materials.

IN ORDER FOR THE FOLLOWING TABLES AND FIGURES TO APPEAR TOGETHER, THIS PAGE IS BLANK.

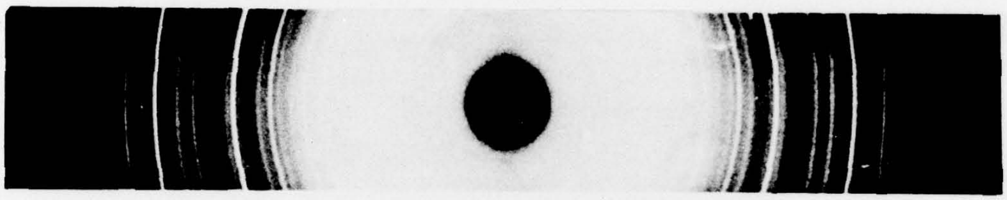


Figure 6. X-ray diffraction spectrum of solid product from Reaction (2). Powder introduced into 0.3 mm capillary. X-ray parameters: 114.6 mm diameter Philips powder camera, no-screen medical x-ray film, Straumanis film technique, CuKα, (Ni filter), 40 kV - 20 MA, 6 hour exposure.

TABLE 7 FIGURE 6—SPECTRUM LINE POSITIONS			TABLE 8 (Si_3N_4) 14H (HIGH TEMP) - SILICON NITRIDE (Possible matches only listed)		
LINE	d(Å)	I/I_1	LINE	d(Å)	I/I_1 (estimate)
1	6.303	5			
2	5.735	80			
3	5.053	2			
4	4.783	90			
5	4.428	20			
6	4.199	100			
7	3.801	2	7	3.82	20
8	3.562	10			
9	3.332	90	9	3.31	85
10	3.048	5			
11	2.979	2			
12	2.876	1			
13	2.718	1.5			
14	2.633	15			
15	2.501	5	15	2.492	100
16	2.329	1			
17	2.284	85			
18	2.224	< 1			
19	2.099	< 1			
20	1.999	3			
21	1.910	5			
22	1.863	< 1			
23	1.796	70			
24	1.753	70	24	1.753	70
25	1.665	8			
26	1.642	< 1			
27	1.591	5			
28	1.571	2			
29	1.539	2			
30	1.477	3			
31	1.453	3			
32	1.395	3			
33	1.375	< 1			
34	1.340	< 1	34	1.358	140
35	1.323	< 1			
36	1.229	1			
37	1.132	1			
38	1.111	< 1			
39	1.082	< 1			
40	1.064	< 1			
41	1.041	< 1			
42	0.995	< 1			

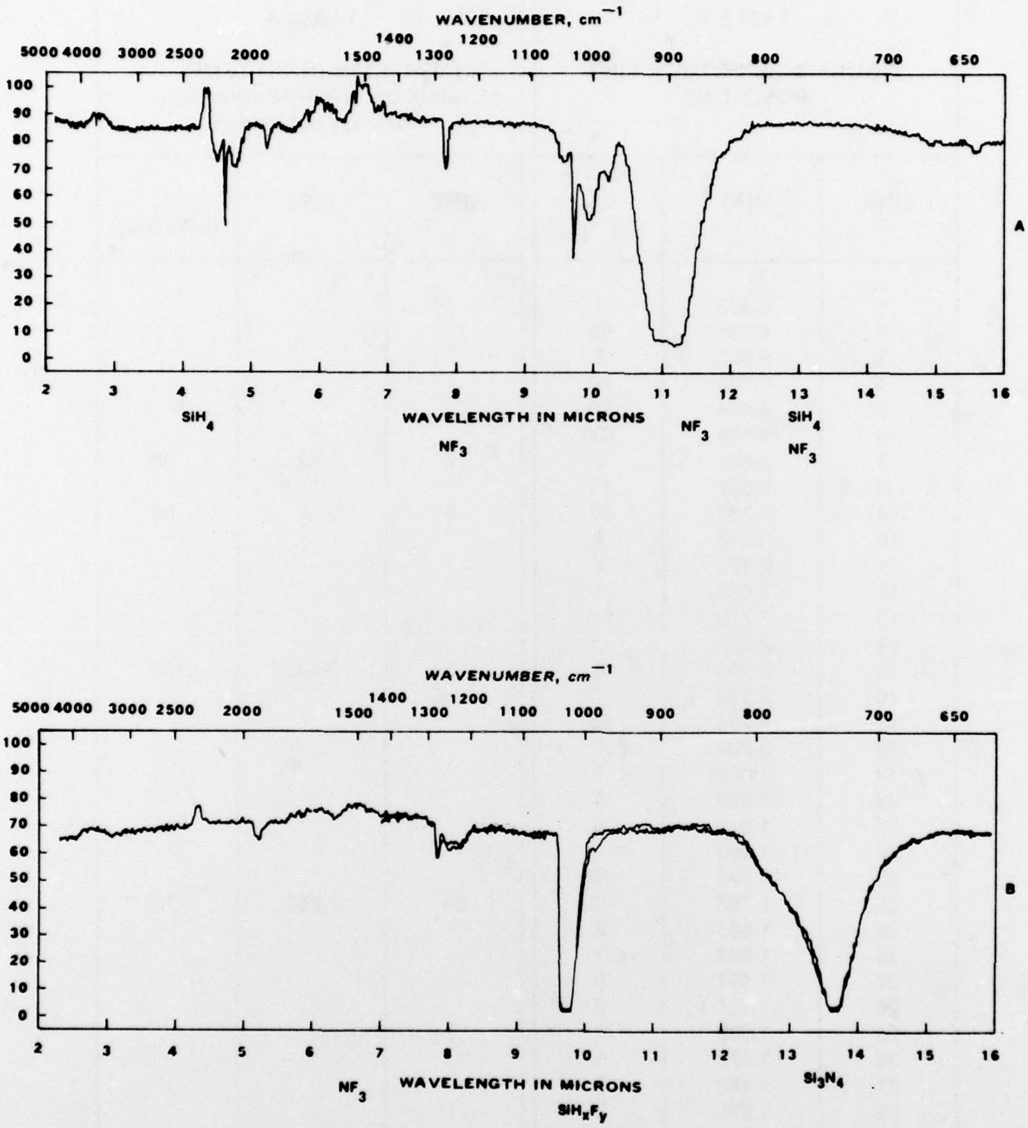


Figure 7. Infrared spectra of the gaseous products of Reaction (2). A: The spectrum before irradiation. B: The products after ≤ 1 sec irradiation time at 35 watts, total pressure 16 torr and excess NF_3.

REFERENCES

1. Popper, P. and Ruddlesden, S. N., Transactions British Ceramic Society, Volume 60, p. 603 (1961).

2. Kaiser, W. and Thurmond, C. D., Journal of Applied Physics, Volume 30, (1959), p. 427.

3. Jenkner, H. and Schmidt, H. W., German Patent 1,136,315 (September 1962).

4. Merritt, J. A., Meyer, H. C., Greenberg, R. I., and Tanton, G. A., "The Production of Decaborane-14 from Diborane by Laser Induced Chemistry", to be published in *Propellants and Explosives*, (Verlag Chemie).

5. Matheson Gas Data Book, Fifth Edition (1971).

6. Yoshiska, S. and Takayanagi, S., Electrochemical Society Journal, Volume 114, (1967) p. 962.

7. Doo V. Y., Nichols D. R., and Silvey G. A., Electrochemical Society Journal, Volume 113, (1966), p. 1279.

8. Bean, K. E., Gelim, P. S., and Yeakley, R. L., Electrochemical Society Journal, Volume 114, (1967), p. 733.

9. Sterling, H. F. and Swann, R. C. G., Solid State Electronics, Volume 8, (1965), p. 653.

DISTRIBUTION

Commander Defense Documentation Center ATTN: DDC-TCA Cameron Station Alexandrix, Virginia 22314	12
Commander US Army Research Office PO Box 12211 Research Triangle Park, North Carolina 27709	1
ATTN: DRXRO-PH, Dr. Lontz	1
DRXRO-C, Dr. Squire/Dr. Houk	1
US Army Research and Standardization Group (Europe) ATTN: DRXSN-E-RX, Dr. George Wyman Box 65, FPO New York 09510	1
US Army Materiel Development and Readiness Command ATTN: Dr. James Bender 5001 Eisenhower Avenue Alexandria, Virginia 22333	1
OUSDR&E ATTN: Mr. Leonard R. Weisberg Room 3D1079, The Pentagon Washington, DC 20310	1
Director Defense Advanced Research Projects Agency 1400 Wilson Boulevard Arlington, Virginia 22209	1
Dr. Frank Verderame Headquarters, DA-ODCSRDA DAMA-ARZ-D Room 3E363, The Pentagon Washington, DC 20310	1

DISTRIBUTION

	No. of Copies
OUSDR&E	
ATTN: Dr. G. Gamota	1
Deputy Assistant for Research	
(Research in Advanced Technology)	
Room 3D1067, The Pentagon	
Washington, DC 20310	
Mr. Sam DeVita	1
Fiber Optics Branch	
CENCOMS	
US Army Communications R&D Command	
ATTN: DRDCO-COM-RM-1	1
Fort Monmouth, New Jersey 07703	
IIT Research Institute	
ATTN: GACIAC	1
10 West 35th Street	
Chicago, Illinois 60616	
US Army Materiel Systems	
Analysis Activity	
ATTN: DRXSY-MP	2
Aberdeen Proving Ground, Maryland 21005	
Ballistic Missile Defense Advanced Technology Center	
ATTN: Mr. Sayles	1
PO Box 1500	
Huntsville, Alabama 35807	
DRSMI-R, Mr. Fagan	1
-RK, Dr. Rhoades	1
-RR, Dr. Hartman	1
-RRD	1
-LP, Mr. Voigt	1
-R, Dr. Kobler	1
-RPR	3
-RPT(Reference)	1
-RPT(Record Set)	1
-EM	1

☆ U.S. GOVERNMENT PRINTING OFFICE; 1980—640-287/244 REGION NO.4