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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

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1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release Distribution unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S) **AFOSR-TR- 86-0570**
6a NAME OF PERFORMING ORGANIZATION Corning Glass Works 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION AFOSR/NC
6c ADDRESS (City, State and ZIP Code) Research & Development Division Corning, NY 14831	7b ADDRESS (City, State and ZIP Code) Bldg 410 Bolling AFB DC 20332-6448
8a NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR/NC 8b OFFICE SYMBOL (If applicable) NC	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-84-C-0098
8c ADDRESS (City, State and ZIP Code) Bldg 410 Bolling AFB DC 20332-6448	10 SOURCE OF FUNDING NOS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT NO
61102F	2303	A3	

11 TITLE (Include Security Classification) Fluoride Glasses for Bulk Optical and Waveguide Applications

12. PERSONAL AUTHOR(S) P. A. Tick

13a. TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Yr, Mo, Day)	15 PAGE COUNT
Final	FROM 15 Aug 84 TO 14 Aug 85	Jan 86	19

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB GR	heavy metal fluoride glass

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

The goal of this project completed under Contract No. F49620-83-C-0090 and F49620-84-C-0098 and sponsored by the Air Force Office of Scientific Research (AFOSR), was to find a wide transmission window fluoride glass which could be compatible with chemical vapor deposition. The intent of the work was to use these glasses for bulk IR optics or for ultra low-loss OWG fibers. A new glass family was discovered and explored under this research program. This new fluoride composition field of CdF_2-LiF-AlF_3-PbF_2 (CLAP) was identified and patented during the study. Potentially, many Air Force requirements both in bulk optics and optical fibers for infrared transmission can be met using this new glass.

During the course of this study, the CLAP glasses were identified, patented, and characterized. CLAP glasses were found

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS ☐	21 ABSTRACT SECURITY CLASSIFICATION

22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE NUMBER (Include Area Code)	22c OFFICE SYMBOL
DONALD R. ULRICH	767-4960	NC

DD FORM 1473, 83 APR EDITION OF 1 JAN 73 IS OBSOLETE

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to have equivalent stability than more commonly used glasses such as the fluorozirconates. CLAP glasses have a slightly reduced transmission window, but this trivial disadvantage is more than made up for by its considerably better resistance to water attack.

To demonstrate these new glasses as an infrared transmitting material, water had to be removed from our initial compositions. Water has strong IR absorption bands in the 2.5 - 3.5 micron wavelength spectral region of operation. This was done with a special RAP furnace made available at Corning (built entirely with Corning funds) to be used for this research. This furnace, along with other specialized equipment such as glove boxes, mixing facilities, and general familiarity with fluoride glass, enabled this research to proceed rapidly to commercialization. Results indicated that $CClF_3$, CCl_2F_2, and $CClF_3$ were effective in removing water.

RAP furnace results showed that in small amounts neither oxygen or chlorine seems detrimental to glass forming. A one percent concentration of both appears to enhance vitreous stability and oxygen alone improves durability.

In more recent work, the effect of rare earths on attenuation was studied. Five fluoride salts of rare earths were doped into a base CLAP glass and the optical spectra was measured at several concentration levels. Results showed Eu and Nd impurities would be harmful to ultra low-loss transmission between 2.5 and 3.5 microns.

In conclusion, the CLAP system represents a new heavy metal fluoride glass family with good stability and excellent resistance to water attack. All the components are compatible with chemical vapor transport. For infrared transmission applications, water can be removed by RAP melting. Small amounts of chlorine and oxygen enhance vitreous stability and Eu and Nd impurities were found to have negative effects on ultra low-loss transmission. Small quantities of this glass are available commercially from Corning Glass Works, Research and Development Division.

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AFOSR-TR- 86-0570

Corning Glass Works
Corning, New York

FLUORIDE GLASSES FOR BULK OPTICAL AND WAVEGUIDE APPLICATIONS

FINAL REPORT

Corning Glass Works
P. A. Tick

Contract No. F49620-84-C-0098

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FLUORIDE GLASSES FOR BULK OPTICAL AND WAVEGUIDE APPLICATIONS

FINAL REPORT

CONTRACT NUMBER F49620-84-C-0098

INTRODUCTION

The overall goal of the research was to develop a wide transmission window heavy metal fluoride glass (HMFG) which could eventually be compatible with chemical vapor deposition (CVD) forming. During the first two years of contract work, a new composition field, i.e., CLAP ($CdF_2 \cdot LiF \cdot AlF_3 \cdot PbF_2$) glasses, were identified and the basic chemistry and properties of the system determined. Since the intent of the work is to use such glasses for bulk IR optics or for ultra-low-loss OWG fibers, further characterization was required.

It remained to establish the utility of these glasses as practical infrared transmitting materials. This required that a method for removing water be found and that the effects of infrared absorbing impurities be determined. Work in these two areas constituted much of the recent effort.

EXPERIMENTAL RESULTS

In order to upgrade the glass quality over that of initial composition survey work, the purity of the batch components was improved. Sources of high-purity PbF_2, LiF, and CdF_2 were found and these materials were used in all of the current experiments. Table 1 shows typical analysis of these materials. Analysis is routinely performed at Corning by atomic absorption techniques that routinely characterize impurities in sub-ppm levels. Although a better source for anhydrous AlF_3 is still being sought, a present supplier of other materials expects high-purity AlF_3 to be available in early 1986.

Glass for the composition experiments was prepared by melting 30g batches under dry nitrogen in 35 ml platinum crucibles at 950°C. It was found that by transferring the hot glass to platinum foil tubes, reheating, and then quenching in hot silicone oil, glass bars 1 cm in diameter by 5 cm long, which are essentially free of crystals, could be obtained. A transmission electromicrograph shown in Figure 1 at 40,000x magnification, confirms the absence of any second phase regions.

The glass bars could be annealed and cut up for further measurements. The details of experimental characterization were described previously.[1]

Viscosity was measured by Professor James Shelby at Alfred University using a microbeam bending technique. The temperature dependence of viscosity is shown in Figure 2. The glass shows normal Arrhenius behavior over about three orders of magnitude in viscosity (10^9-10^{12} poise).

In another set of experiments, the effects of chlorine and oxygen were examined by introduction of $29CdF_2 \cdot 9LiF \cdot 35AlF_3 \cdot 29PbF_2$. Previous analytical work confirmed the presence of ca. 0.5 w/o O as an impurity in glasses melted <u>without</u> RAP conditions. This experiment established the effect prior to our RAP experiments. Small substitutions, up to about one weight percent, improved glass quality. Tg was lowered when chlorine was present and increased with increasing oxygen. Durability improved at higher oxygen concentrations. The multiphonon edge was shifted toward shorter wavelengths with increasing oxygen concentration and unaffected by chlorine. This is shown in Figure 3. These results are consistent with previous results for the ZBLA system.

Five rare-earth elements, Nd, Sm, Pr, Er, and Eu, were doped into a glass of composition $29.5CdF_2 \cdot 8.5LiF \cdot 34.5AlF_3 \cdot 27.5PbF_2$, then formed into quenched bars and the transmission spectra measured. Figure 4 shows the details of spectral structure associated with each rare-earth dopant. The plot of absorption coefficient for several rare-earth transitions as a function of concentration (Figure 5) demonstrates Beer-Lambert behavior. Since the spectral region between 2.6 and 3.5 microns is where OWG of these glasses will transmit for minimum attenuation, only the absorption peaks in this vicinity are important. Those are shown in Table 2. The absorption wavelength, absorption coefficient, and specific attenuation for each of the transitions involved are shown. Since it is not known whether the line shape of the decay of each peak was Gaussian or Lorentzian, the effect of both shapes at 2.6 and 3.5 microns was computed. The proximity of transition peaks of Nd and Eu make these two rare earths the most serious obstacles to ultra-low attenuation in these glasses. The attenuation values (dB/km ppmw) tend to be slightly larger than those reported for fluorozirconate glasses.[2]

The construction of a furnace, capable of reactive atmosphere processing (RAP melting) up to 1 kg of glass, was completed in mid-1985. A schematic diagram and a photograph of the apparatus are shown in Figure 6. RAP experiments were conducted with a 350g batch of $25.5CdF_2 \cdot 8.5LiF \cdot 34.5AlF_3 \cdot 27.5PbF_2$ glass, which was placed in a covered platinum crucible then lowered into the furnace enclosure. The melt was then heated in flowing nitrogen to 950°C by inductively coupling to the platinum crucible. Once at temperature, a RAP gas could be introduced directly <u>above</u> the melt surface. After completing a RAP cycle, the hot glass was transferred to smaller platinum containers where it was remelted and cast into bars or patties.

Five RAP gases were tested to date. These include CF_4, NF_3, $CClF_3$, CCl_2F_2, and CCl_3F. Relative water concentrations in the final glasses were monitored by the intensity of the water band at 2920 nm; the results of the preliminary evaluation of these five gases is summarized in Table 3. The base line absorption coefficient should lie between 1.8 and 8 μm^{-1}, as estimated from a number of 30g melts in which no RAP was done. The CF_4 gas seems to be completely ineffective while NF_3 seems to be at best, very inefficient. Surprisingly, just a high flow of nitrogen itself seems to be fairly effective in removing water. All of the chlorine-containing gases appear to be very efficient in removing the hydroxyl associated with the 2920 nm band. For example, Figure 7 shows the changes in both the 2920 nm as well as a second band at 5400 nm as exposure time to relatively low flows of $CClF_3$ increases. The absorption coefficient decreases by about a factor of two every fifteen minutes. In another experiment, a glass treated with CCl_2F_2 for one hour at a faster flow rate showed no evidence of the 2920 nm hydroxyl band.

DISCUSSION

The CLAP system represents a new HMFG family. It is comparable in stability to fluorozirconates, has a somewhat smaller transmission window and is considerably more resistant to water attack. It also provides a system in which each of the components is compatible with chemical vapor transport.

The emphasis on the more recent work was to assess the utility of these glasses for both bulk optics and optical waveguide applications. The attenuation of various rare-earth transitions appear to be slightly larger in these glasses than those reported for the fluorozirconates, which is a slight disadvantage. Eu and Nd appear to be the most serious of the rare-earth impurities. Preliminary RAP melting experiments have shown that the chlorine-containing gases, $CClF_3$, CCl_2F_2, and CCl_3F are all effective water getters while NF_3 and CF_4 are not. CCl_4 would probably also be effective, but it, like CCl_3F, is a liquid at room temperature and would require a bubbler, whereas the other compounds are gases at room temperature. The actual efficiencies of each of the gases will still have to be determined.

In small amounts of the order of 1%, neither Cl nor oxygen seems to be detrimental to glass forming. Oxygen improves the durability but shifts the multiphonon edge towards the visible.

REFERENCES

1. P. A. Tick, D. A. Thompson and F. J. Quan, Annual Report, Contract F49620-83-C-0090, August 31, 1984.

2. Y. Ohishi, S. Mitachi, S. Shibata and T. Manabe, Jap. J. Appl. Phys., 20, March 3, 1981, pp. L191-L193.

TABLE 1

PURITY OF NEW HIGH-QUALITY BATCH MATERIALS FOR CLAP GLASSES

Compound	Impurities ppb*					
	Fe	Cr	Cu	Mn	Ni	Al
PbF_2	173	79	406	<85	74	<128
LiF	26	39	2816	14	<55	255
CdF_2 (Supplier 1)	<155	368	943	<22	<69	<109
CdF_2 (Supplier 2)	<204	505	1125	<29	<91	<143

*All values analyzed by Corning Glass Works.

TABLE 2

EXTRAPOLATED OPTICAL EFFECTS OF RARE EARTHS

	Absorption Peak				Estimated Attenuation dB/km ppmw			
					2.6 microns		3.6 microns	
Dopant	Wavelength nm	Attenuation dB/km ppmw	Band Width At Half Intensity nm	Transition	Gaussian	Lorentzian	Gaussian	Lorentzian
Eu	3350	17.0	200	$^7F_0-^7F_4$	Negligible	.27	3.57	5.23
Eu	2200	11.9	35	$^7F_1-^7F_6$	Negligible	.02	Negligible	.002
Eu	2080	17.0	85	$^7F_0-^7F_6$	Negligible	.11	Negligible	.015
Pr	2330	19.0	100	$^3H_4-^3H_6$	Negligible	.63	Negligible	.034
Pr	1940	34.7	125	$^3H_4-^3F_2$	Negligible	.31	Negligible	.056
Nd	2550	23.6	240	$^4I_{9/2}-^4I_{13/2}$	20.9	20.1	Negligible	.37

TABLE 3

EFFECT OF RAP GAS UPON THE WATER BAND AT 2920 nm IN 29.5 $CdF_2 \cdot 8.5\ LiF \cdot 34.5\ AlF_3 \cdot 27.5\ PbF_2$

RAP Gas	Temperature °C	Exposure Time mm	Flow Rate Relative	α cm^{-1}
None*	950°	-	-	1.83→ 8.04
N_2	950°	30	10	.153
N_2	950°	45	10	.164
10% NF_3 in N_2	950°	15	4	.619
10% NF_3 in N_2	950°	30	4	1.694
10% NF_3 in N2	950°	36	4	.534
10% CF_4 in N_2	950°	30	10	3.54
10% CCl_2F_2 in N_2	950°	15	2	.221
10% CCl_2F_2 in N_2	950°	30	2	.301
10% CCl_2F_2 in N_2	950°	45	2	.098
10% CCl_3F in N2	950°	15	2	.290
10% CCl_3F in N_2	950°	30	2	.094
10% $CClF_3$ in N_2	950°	15	4	.522
10% $CClF_3$ in N_2	950°	30	4	.177
10% $CClF_3$ in N_2	950°	45	4	.098

Data taken from eleven 30 g melts prepared under dry N_2, and melted for 15 minutes at 950°C.

TABLE 4

SPECIFICATIONS AND PROPERTIES OF RAP GASES

Gas	Supplier	Boiling Pt. °C (760 Torr)	Purity (Grade)
N_2	House nitrogen		~98%
NF_3	Air Products	-129.06°C	Technical 98.0 wt%
CF_4	Air Products 10% Halocarbon - 14 in N_2	-128°C	Semiconductor 99.9%
$CClF_3$	Air Products 10% Halocarbon - 13 in N_2	-81.2°C	C.P. Grade 99.0% (liquid phase)
CCl_2F_2	Air Products 10% Halocarbon - 12 in N_2	-29.9°C	C.P. Grade 99.0% (liquid phase)
CCl_3F	Air Products 10% Halocarbon - 11 in N_2	23.77°C	C.P. Grade 99.9% (liquid phase)

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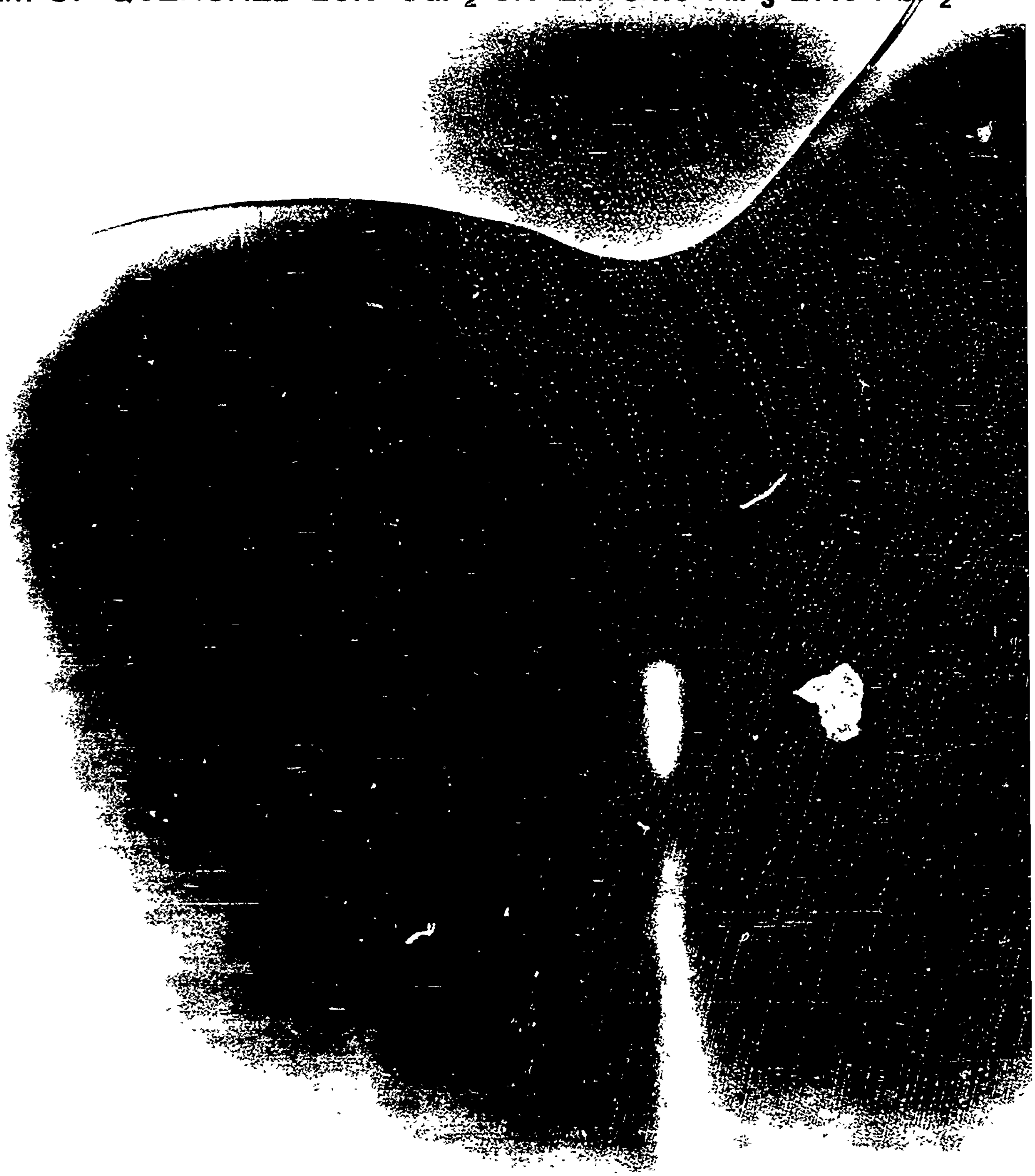
FIGURE 1.

TEM OF QUENCHED 29.5 CdF_2·8.5 LiF·34.5 AlF_3·27.5 PbF_2



741 40,000x

140-85 RLM-741

FIGURE 2.

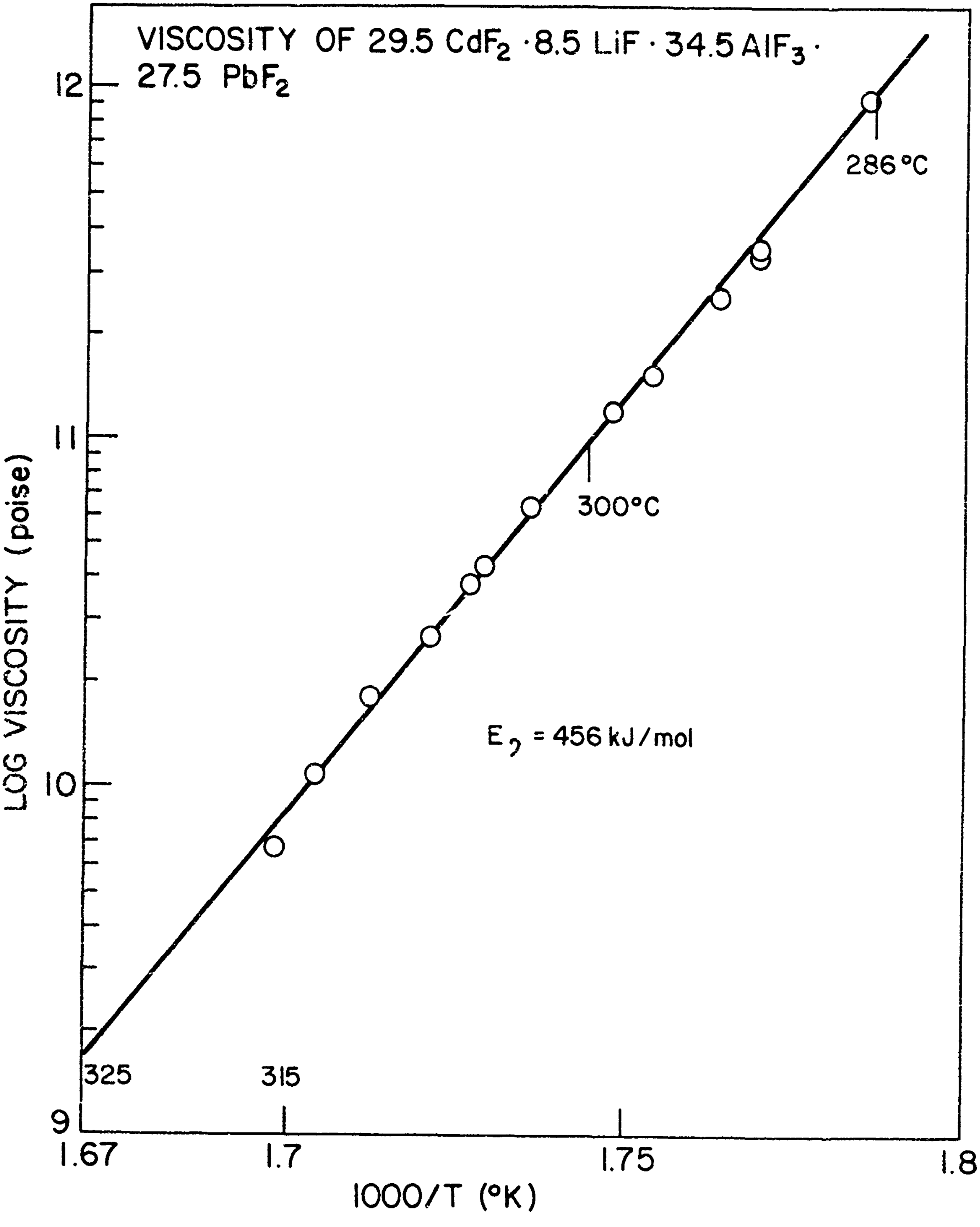

VISCOSITY OF 29.5 CdF₂ · 8.5 LiF · 34.5 AlF₃ · 27.5 PbF₂
12
11
10
9
LOG VISCOSITY (poise)
286 °C
300 °C
E₂ = 456 kJ/mol
325
315
1.67
1.7
1.75
1.8
1000/T (°K)

FIGURE 3.
IR TRANSMISSION OF OXYGEN AND CHLORINE DOPED SAMPLE

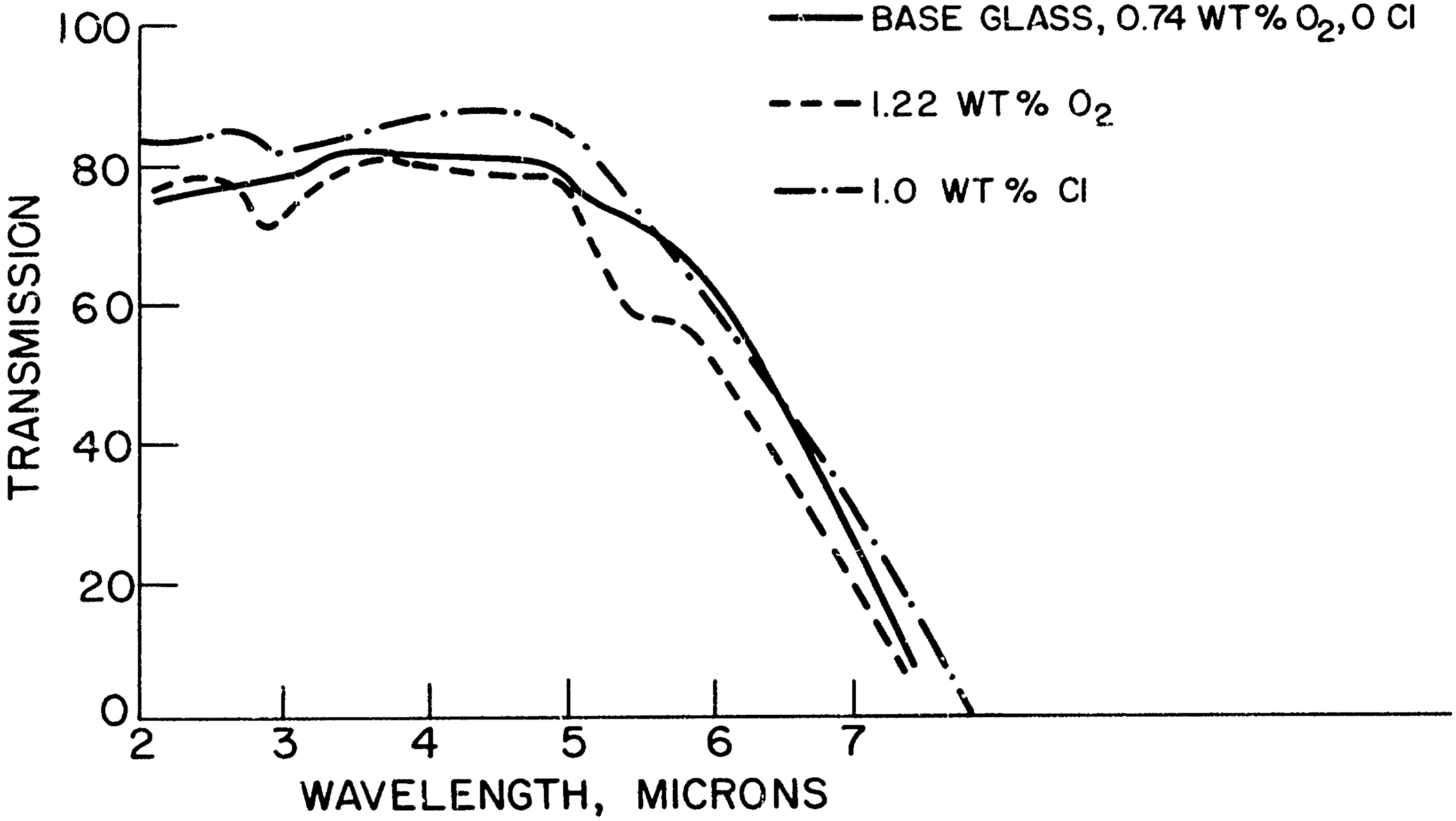


FIGURE 4.
SPECIAL TRANSMISSION CHARACTERISTICS OF RARE EARTH DOPED CLAP GLASSES

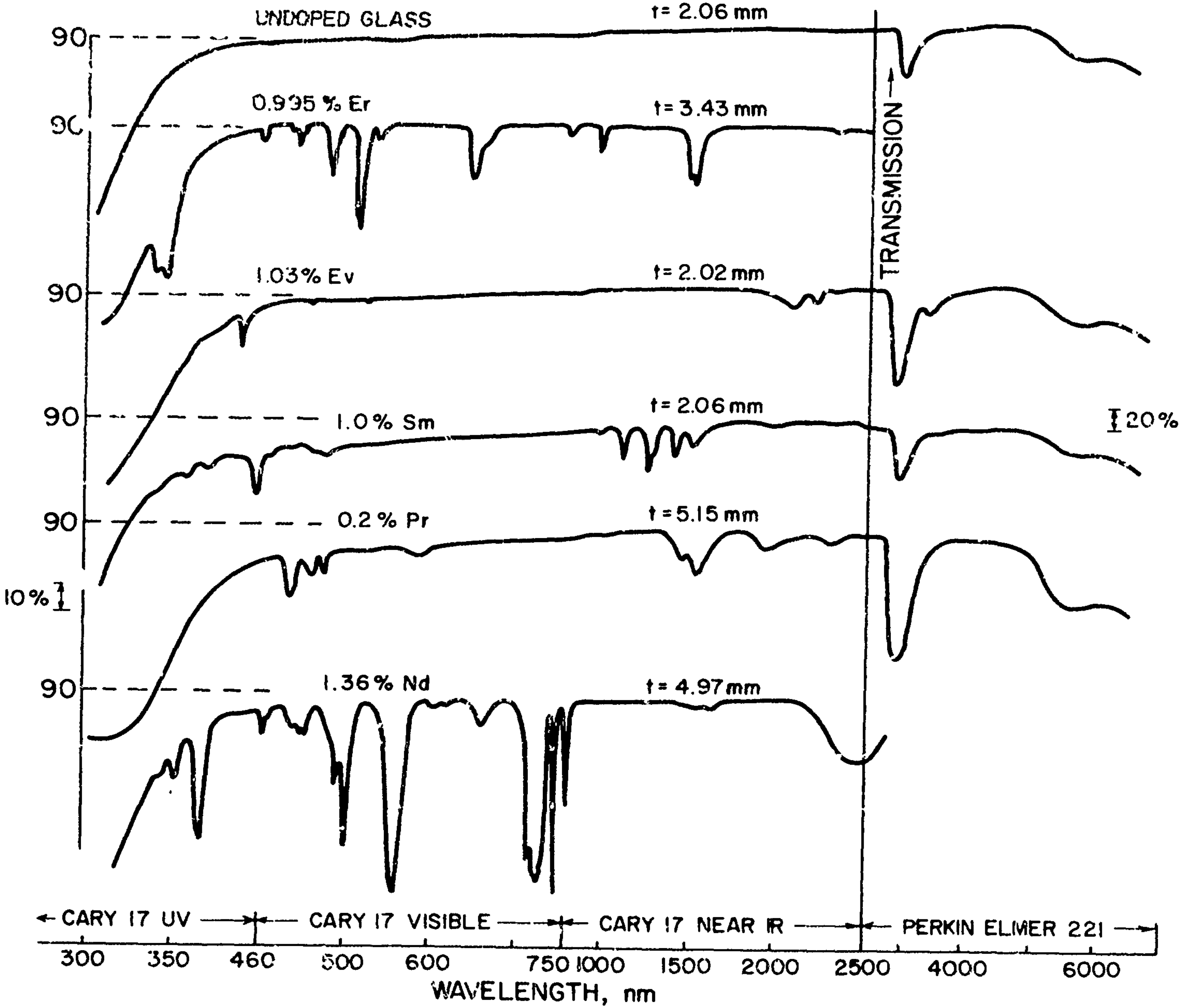


FIGURE 5.
CONCENTRATION DEPENDENCE OF ABSORPTION FOR SELECTED RARE EARTH ABSORPTION PEAKS IN $29.5\ CdF_2 \cdot 8.5\ LiF \cdot 34.5\ AlF_3 \cdot 27.5\ PbF_2$

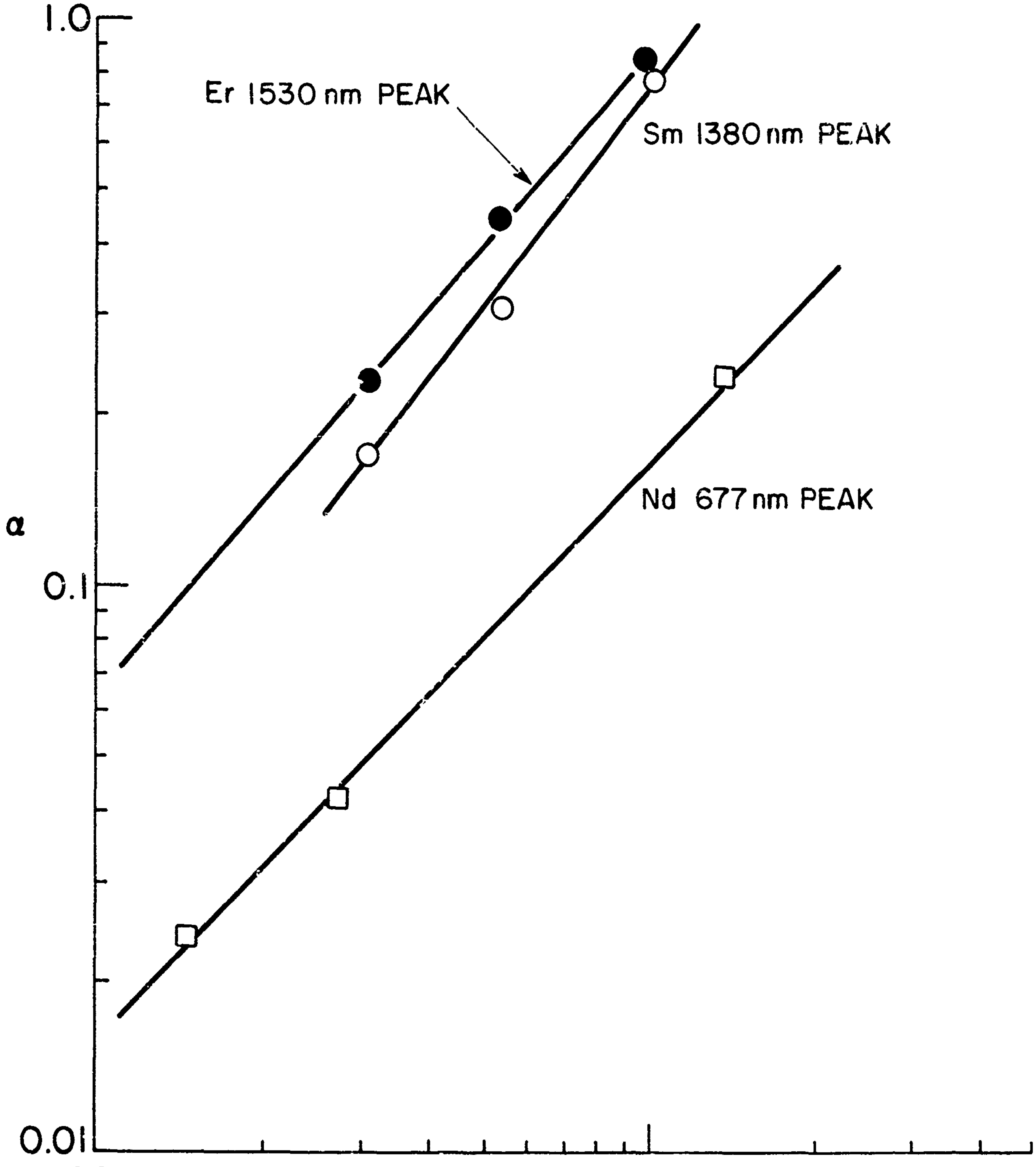
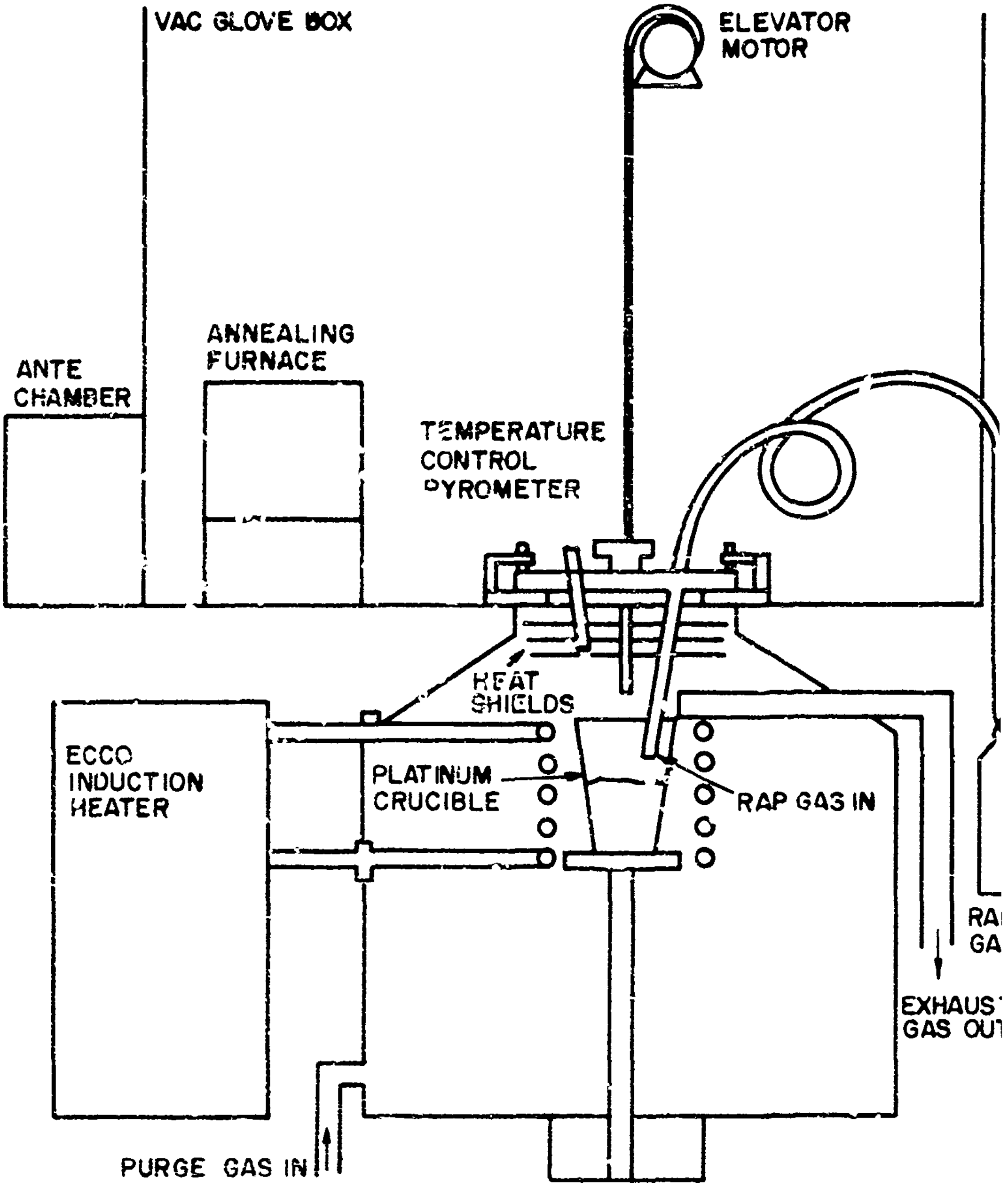


FIGURE 6.
MELTING FURNACE

A. SCHEMATIC



B. PHOTOGRAPH

FIGURE 7.
EFFECT OF $CClF_3$ ON WATER CONTENT IN 29.5 CdF_2 · 8.5 LiF · 27.5 PbF_2 · 34.5 AlF_3

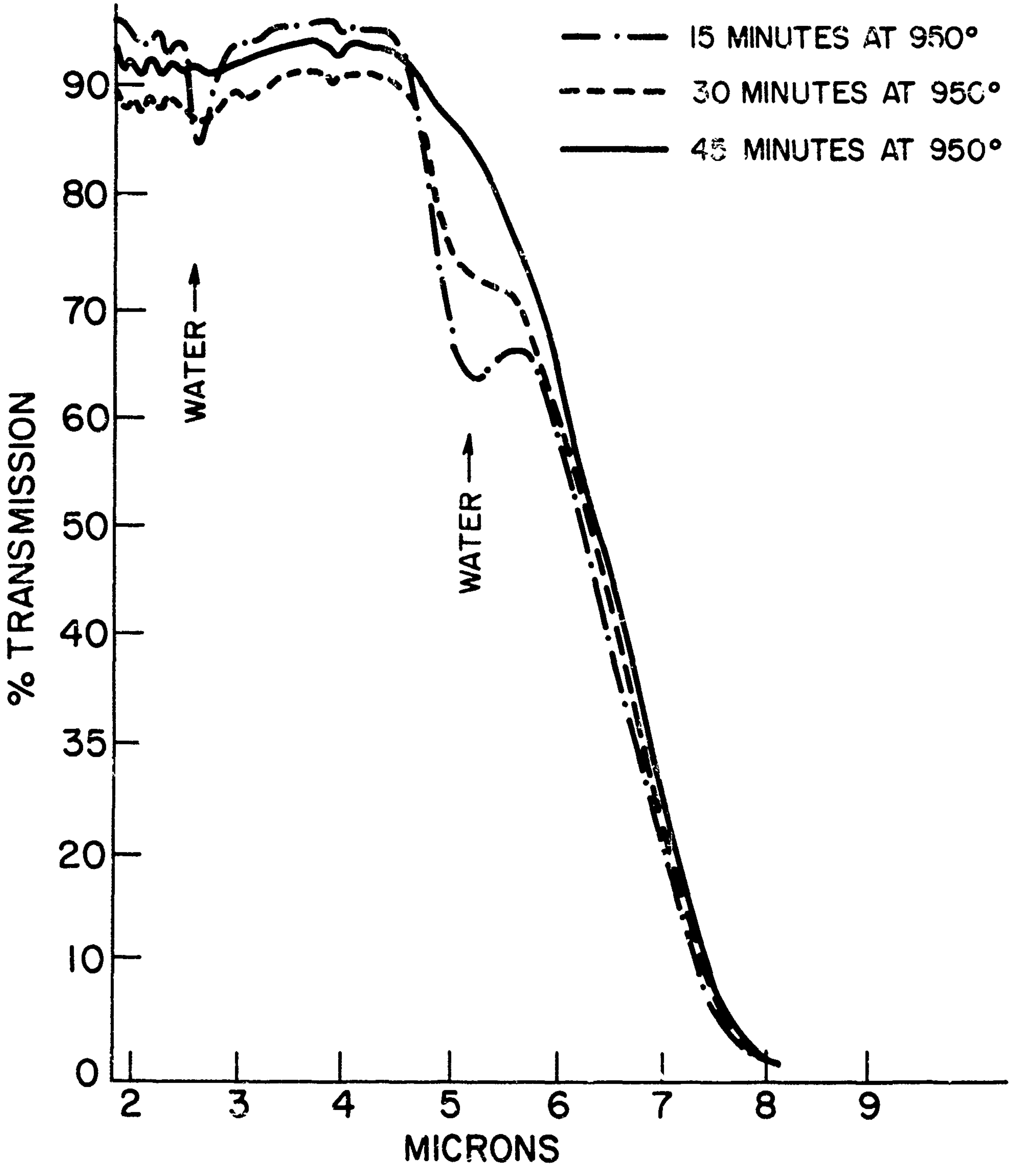


FIGURE 8.
IR SPECTRAL TRANSMISSION OF 29.5 CdF_2 · 8.5 LiF · 27.5 PbF_2 · 34.5 AlF_3 TREATED WITH CCl_2F_2 FOR 1 HOUR AT 950°.