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LOW LOSS LASER GLASS

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TABLE OF CONTENTS

	<u>PAGE</u>
1. INTRODUCTION	1
2. EVALUATION OF LOSS FACTORS	1-2
3. EXPERIMENTAL PROCEDURES	2
3.1. GLASS COMPOSITION	2
3.2. PURIFICATION OF RAW MATERIALS	2-3
3.3. BATCH PREPARATION	3
3.4. MELTING	3-4
4. RESULTS AND DISCUSSIONS	4
4.1. BATCH MATERIALS	4
4.1.1. RAW MATERIALS	4
4.1.2. PURIFICATION OF P ₂ O ₅	4-5
4.2. CRUCIBLE MATERIALS	5-6
4.3. MELTING FURNACE	6
4.4. DEHYDRATION	6-7
4.5. CONTRIBUTION OF EACH LOSS FACTOR	7-8
4.6. 0.5 LITER MELTING	8-9
5. SUMMARY	10-11
REFERENCES	12
TABLE 1 BATCH MATERIALS AND THEIR ESTIMATED CONTRIBUTION TO THE LOSS OF THE GLASS	13
TABLE 2 MELTING CONDITIONS AND ABSORPTION AT 1.05μ FOR 80 g MELTS	14
TABLE 3 IMPURITY IN CRUCIBLE MATERIALS AND DISSOLUTION RATE OF IMPURITY INTO GLASS MELT	15
TABLE 4 EFFECT OF OH CONTENT, Pt ION CONCENTRATION AND CONTAMINATION TO LOSS AT 1.05μ	16
FIGURE 1 LOSS FACTOR	17
FIGURE 2 VAPOR PRESSURES OF FLUORIDES AND CHLORIDES OF LASER GLASS BATCH COMPONENTS AND SOME TRANSITION METAL IMPURITIES	18
FIGURE 3 SUBLIMATION EQUIPMENT FOR P ₂ O ₅	19
FIGURE 4 EFFECT OF MELTING CONDITION TO Fe ³⁺ /Fe ²⁺ RATIO	20
FIGURE 5a EFFECT OF CARRIER GAS COMPOSITION	21
5b EFFECT OF ATMOSPHERE CONTROL GAS COMPOSITION	21
5c EFFECT OF DEHYDRATION TEMPERATURE	21
5d EFFECT OF REFINING TEMPERATURE	21
FIGURE 6 ABSORPTION SPECTRA OF HIGHLY WATER CONTAINING GLASS	22

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1. INTRODUCTION

The objective of this work was a process development on making a laser glass with loss coefficient of 10^{-6}cm^{-1} at 1.05μ . The key issues for making such a low loss glass will be to use pure raw materials, to reduce OH content and to prevent contamination from the melting environment. A sublimation method was tried to prepare pure P_2O_5 batch material. In an attempt to distinguish contributions to the overall loss, glasses were melted in furnaces which were controlled in moisture as well as contamination. Evaluation of glass samples at LLNL are expected to provide guidance on the importance of various process parameters. A new 0.5 liter furnace which almost completely prevents contamination by the furnace environment has been constructed to obtain useful information for making a low loss glass on a production scale.

2. EVALUATION OF LOSS FACTORS

Various factors which affect the loss at 1.05μ are summarized in Figure 1. Among them, the intrinsic absorption and scattering can contribute to the loss at 1.05μ only by about 10^{-6}cm^{-1} . The Mie scattering due to bubbles, seeds and Pt inclusions¹⁾ will be also negligible in a glass with laser quality. Accordingly, the loss due to impurities such as transition metal ions, lanthanide ions, Pt ions and OH ions will be major factors. The contributions of Fe and Cu to the loss at $1.05\mu\text{m}$ were

estimated as $0.007 \times 10^{-4}/\text{cm}$ ppb and $0.023 \times 10^{-4}/\text{cm}$ ppb, respectively in phosphate glasses. ²⁾ Ni and Co are also effective to the loss. ²⁾³⁾ Lanthanide ions such as Dy^{3+} , Pr^{3+} and Sm^{3+} are much less effective to the loss at 1.05μ compared to transition metal ions. The contribution of OH absorption to the loss at 1.05μ has not been evaluated in phosphate glass, but it is expected to be important based on the data of SiO_2 optical fibers.⁴⁾ The loss due to Pt ion absorption has not been determined yet.

Therefore, the key issues to make low loss glass are to use pure raw materials, to prevent contamination by transition metal ions from the furnace environment, to reduce OH content and to suppress Pt ion dissolution from the crucible.

3. EXPERIMENTAL PROCEDURES

3.1. GLASS COMPOSITION

A simple composition consisting of three components, 65 P_2O_5 -12.5 Al_2O_3 -22.5 Na_2O in mol %, was chosen because highly pure raw materials were easily obtainable.

3.2. PURIFICATION OF RAW MATERIALS

In-house preparation of highly pure raw materials is desirable in many aspects, if sufficiently simple techniques can be found to purify purchased reagent grade starting materials. Sublimation is a useful purification method if the following conditions are fulfilled:

1. Sufficient partial pressure of sublimand to yield a practical rate of sublimation.
2. Efficient condensation to yield a solid sublimate.
3. Large surface area of sublimand.
4. Impurities of low volatility at sublimation condition.

Figure 2 shows the vapor pressures of some oxides, fluorides and chlorides. P_2O_5 appears to be a prime candidate for purification by sublimation at about $360^\circ C$. In addition, $AlCl_3$ can be sublimed at about $180^\circ C$, leaving $FeCl_3$ and $FeCl_2$ in the residue. $NbCl_5$ may be sublimed at about $250^\circ C$. The sublimation equipment for P_2O_5 is illustrated in Figure 3. 1 kg granular P_2O_5 is added in the 5 liter flask and heated up to about $300^\circ C$ under flowing dry N_2 gas. The sublimed P_2O_5 is collected in a 4 liter collection bottle.

3.3. BATCH PREPARATION

The batch components are weighed and mixed to a slurry in a teflon or polyethylene container in a clean room area. Water and decomposed gases are driven off in a fused quartz beaker at temperatures ranging up to about $400^\circ C$, in some cases. Care is taken to keep contamination to a minimum.

3.4. MELTING

Mixed batch is transferred into a fused quartz crucible in the melting chamber. Melting at small scale (80g and 250g) is performed with batch loading, dehydration and refining. Glass is cast into a graphite mold.

These small scale melts were made in an attempt to distinguish contributions of water content, contamination from crucible materials and furnace environment and impurities in batch materials to the overall measured loss.

4. RESULTS AND DISCUSSIONS

4.1. BATCH MATERIALS

4.1.1. RAW MATERIALS

Cu^{2+} and Fe^{2+} ions are most effective for absorption loss at $1.05\mu\text{m}$ in phosphate glasses. ²⁾³⁾ Concentrations of these ions should be lower than about 43 ppb and 143 ppb, respectively. ²⁾ Although these values are not necessarily true for glasses with different compositions, these will provide reasonably good guidance. Using the suppliers' data of specified or analyzed contents of Fe and Cu impurity, it is seen in Table 1 that the target value of $1 \times 10^{-4}\text{cm}^{-1}$ is just exceeded, assuming the maximum specified impurity levels. However, the contribution of Fe to the absorption loss at $1.05\mu\text{m}$ will be less because the glass will be melted in a highly oxidized condition to remove Pt inclusions and a certain amount of Fe^{2+} is turned to Fe^{3+} ion which does not have absorption at 1.05μ as shown in Figure 4.

4.1.2. PURIFICATION OF P_2O_5

P_2O_5 begins to sublime at 250°C , appearing as a slowly falling crystalline dust which becomes flake like at around 300°C . Work inside of a dry box and very dry

gas would increase the presently low yield. The chemical analysis of the sublimed sample is being done at LLNL.

4.2. CRUCIBLE MATERIALS

One of the possible contamination sources during melting is the dissolution of impurities from the crucible. Table 3 shows the 80g melts for distinguishing this contribution. Important issues which can be resolved by measurement of loss and by chemical analysis are:

- How much transition metal impurities are introduced by the fused quartz, Pt 99.99% and Pt 99.95% crucibles respectively?
- What is the effect of oxygen gas and special kind of oxidizing gas for producing Pt inclusion free glass in Pt crucible to the loss?

The dissolution rates of Pt and fused quartz crucibles are listed in Table 3. Transition metal impurities dissolved from crucibles are expected to be less than a few ppb. Therefore, this will not affect the overall loss.

The absorption spectra measurement of samples showed much higher loss at 1.05μ than expected from the impurity content of batch materials as shown in Table 1. There seems to be some trend in loss between crucible material, and gas treatment. However, it will not be so useful to explain the result because the loss is very high for all samples, that is, glass might have been accidentally contaminated. One of the potential contamination sources is raw material, especially H_3PO_4 which claims less than 50 ppb of Fe and Cu.

Chemical analysis of raw materials is being performed at LLNL.

4.3. MELTING FURNACE

Three furnaces with different structure have been constructed to prevent contaminations of furnace environment and used for the experiments. All furnaces have muffled structures to control the atmosphere inside of furnaces. The first one was designed for 50 and 200cc crucible melts in which most experiments were made. The second one has a production-like structure with melting zone and stirring zone which has 0.5 liter melting capacity. This furnace was used for the dehydration experiment. The third one is the same as the second one, except for provisions for much more reduced contamination of the furnace environment. Almost half of the project time was spent on the design and set-up of this furnace. The experiment using this furnace, however, has not been completed because devitrification of glass made further melting impossible.

4.4. DEHYDRATION

The process variables which affect water content of glass were investigated. Dehydration was made by bubbling a specific gas carried by gas mixture of N_2 and O_2 through glass melt. Atmosphere inside furnace was controlled by flowing gas mixture of N_2 and O_2 during dehydration. Figure 5a shows the effect of N_2/O_2 ratio of carrier gas for a dehydration reagent. Water content decreases with increasing N_2/O_2 ratio of carrier gas.

However, the effect of carrier gas composition is not observed for another dehydration reagent. Figure 5b shows that water content is constant and independent of N_2/O_2 ratio of atmosphere control gas. Figure 5c shows that water content decreases with increasing dehydration temperature. On the other hand, water content does not change with refining temperature as shown in Figure 5d. Therefore, higher dehydration temperature, dry furnace atmosphere and higher mass flow rate of dehydration reagent, of course, are important to obtain low water containing glass.

4.5. CONTRIBUTION OF EACH LOSS FACTOR

The effect of water content, Pt ion concentration and contamination from the furnace environment to the loss at 1.05μ was investigated. 250g of glass was melted in a fused quartz crucible under flowing O_2 gas at $1200^\circ C$, for 2 hours except for two melts. The melting conditions and preliminary results of loss at 1.05μ are shown in Table 5. A loss at 1.05μ due to OH absorption has not been reported in phosphate glass. Glass samples LL-10 to LL-13 in Table 5 have different water content but same potential contamination from the furnace environment. Preliminary results by transmission spectra measurements, however, showed no trace of absorption at 1.05μ except a very highly water containing glass ($k_2 \cdot 35\mu \geq 30 \text{ cm}^{-1}$) as shown in Figure 6, although the detection is about $3 \times 10^{-4} \text{ cm}^{-1}$.

Therefore, more accurate loss measurement at 1.05 μ is required to clarify the effect of water.

Glass samples LL-16 and LL-17 show the effect of Pt ion to loss at 1.05 μ . Water content and contamination from furnace environment were tried to be held constant for both glasses. Transmission spectra measurement showed again no trace of absorption at 1.05 μ even in a glass containing 500 ppm of Pt. The effect of Pt ion has to be clarified by more accurate loss measurement.

In an attempt to evaluate contamination from furnace environment during melting, glass samples LL-14 and LL-15 were melted for 7 hours and 17 hours. Transmission spectra measurement showed no trace of absorption at 1.05 μ . More accurate measurement is required to distinguish contamination from furnace environment.

In this series of experiments, the effect of water content, Pt ion concentration and contamination from environment to loss at 1.05 μ have not been observed. More accurate loss measurement being done at LLNL will distinguish them.

4.6. 0.5 LITER MELTING

Melting glass has been tried in a newly constructed 0.5 liter furnace which was designed to minimize contamination from furnace environment. After glass was melted down, it was allowed to flow into the fining chamber, then homogenized by stirring. However, glass devitrified inside of the casting orifice. It made a further experiment impossible in this experimental period. This furnace,

however, should produce a quite low loss glass in a production like melting procedure.

We would like to continue the experiment in the next project phase.

5. SUMMARY

Various parameters which affect to the loss at 1.05μ were discussed experimentally. One of the most important parameters is the purity of batch material. The purest raw materials which are commercially available were employed. Loss at 1.05μ estimated from the specified impurity content of raw material was less than $2.7 \times 10^{-4}\text{cm}^{-1}$ and may already exceed the target value of $1 \times 10^{-4}\text{cm}^{-1}$, although the actual impurity content could be much lower than the specified value as being suggested by comparison between specified value and analytical value for one raw material. The second important parameter was expected to be contamination from furnace environment during melting. Special furnaces were constructed to eliminate the contamination. In an attempt to distinguish contribution of contamination by crucible material, and furnace environment, water content and Pt ion concentration of glass to the overall measured loss at 1.05μ , small melts (80g to 250g) were made. The effect of crucible material was not clear because of unexpected high loss, maybe, due to the accidental contamination of purchased raw material. The effects of contamination by furnace environment, water content and Pt concentration of glass were not distinguished because the loss at 1.05μ was below the detection limit of transmittance measurement in all glasses. This result, however, is very encouraging for making low

loss glass and more accurate measurement is expected at LLNL.

Some study on purification of raw material was done. This is very important to make glass with much lower loss at 1.05 μ . Purification of P_2O_5 by sublimation seemed to be a potentially scalable process. Some other materials such as $AlCl_3$, $NbCl_5$ are also easily purified by sublimation. Scale-up melting low loss glass in 0.5 liter capacity furnace was not completed due to devitrification of glass. However, this furnace could make reasonably low loss glass. Therefore, we believe this furnace should be used in the next phase program.

References:

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3. T. Akamatsu, J. Lightwave Tech. LT-1, 580 (1983).
4. P. Kaiser et. al. J. Opt. Soc. Am. 63, 1141 (1973).

TABLE 1 Batch materials and their estimated contribution to the loss of the glass
 65 P₂O₅ - 12.5 Al₂O₃ - 22.5 Na₂O (in mol %)

Amount and type of batch material	Content of transition metal impurity (in ppb)				Contribution of transition metal impurity to batch (in ppb)				Estimated contribution to absorption loss in glass b) (in 10 ⁻⁴ cm ⁻¹)			
	Fe	Cu	Ni ^{a)}	Co ^{c)}	Fe	Cu	Ni	Co	Fe	Cu	Ni	Co
72.3 wt% H ₃ PO ₄	<50	<50	<50	<50	<36	<36	<36	<36				
9.3 wt% Al(OH) ₃	<100 ^{a)}	<50	<50	<50	< 9	< 5	< 5	< 5				
18.4 wt% NaNO ₃	< 5 ^{a)}	< 1	< 1	< 1	< 1	< 0.2	< 0.2	< 0.2				
In 100% Batch					<46	<41.2	<41.2	<41.2				
In glass d)					<80	<72	<72	<72	<0.56	<1.66	<0.20	<0.2
Estimated loss due to batch materials									<2.70			
Target Value									<1.0			

a) Actual lot analysis by manufacturer, about 1/3 of product specification.

b) Using extrapolated effects for Fe: 0.007x10⁻⁴/cm-ppb, Cu:0.023x10⁻⁴/cm · ppb,
 Ni: 0.0028x10⁻⁴/cm · ppb and Co: 0.0035 x 10⁻⁴/cm · ppb⁴⁾

c) Assuming the same content of Co and Ni as Cu

d) 100g glass out of 174.2g batch materials

TABLE 2 Melting conditions^{*)} and absorption at 1.05 μ for 80g melts

	Crucible			Gas Treatment			Absorption ^{a)}	Absorption ^{b)}
	SiO ₂	Pt 99.95	Pt 99.99	Ambient	O ₂	Special Oxidizing Gas	@ 1.05 μ (10 ⁻³ cm ⁻¹)	@ 1.44 μ (10 ⁻³ cm ⁻¹)
LL-1	+			+			---	---
2	+			+			4.3	13.1
3	+			+			---	---
4	+				+		3.6	7.5
5	+					+	0.5	2.9
6		+				+	3.8	1.5
7			+			+	2.1	3.5
8		+			+		2.4	6.1
9			+		+		1.3	5.2

a) Absorption loss expected from batch impurity is less than $0.27 \times 10^{-3} \text{ cm}^{-1}$
(These values were measured by LLNL)

b) Due to overtone of OH absorption band at 2.9 μ
(These values were measured by LLNL)

*) Melting was done at 1200^oC, for 1 hr. including 20 min of gas treatment

TABLE 3 Impurity in crucible materials and dissolution rate of impurity into glass melt

		99.95% Pt	99.99% Pt	Fused quartz (transparent)
Impurity (ppm)	Fe	20	2	1
	Cu	5	1	0.16
Dissolution rate of crucible in LHG-8 melt at 1200°C (cm/sec)		1.1×10^{-9}		2.3×10^{-7}
Dissolved impurity from crucible during 1 hr melt per unit surface area (g/cm ² ·hr)	Fe	1.7×10^{-9}	0.17×10^{-9}	2.0×10^{-9}
	Cu	0.43×10^{-9}	0.08×10^{-9}	0.3×10^{-9}
Totally dissolved impurity during 2 hr in 80g melt (g) ¹⁾	Fe	1.7×10^{-7}	0.17×10^{-7}	2.0×10^{-7}
	Cu	0.43×10^{-7}	0.08×10^{-7}	0.3×10^{-9}
Impurity content in 80g glass (ppb)	Fe	2.1	0.2	2.5
	Cu	0.5	0.1	0.4

1) Surface area of crucible is assumed as 50 cm²

TABLE 4 Effect of OH content, Pt ion concentration and contamination to loss at 1.05 μ

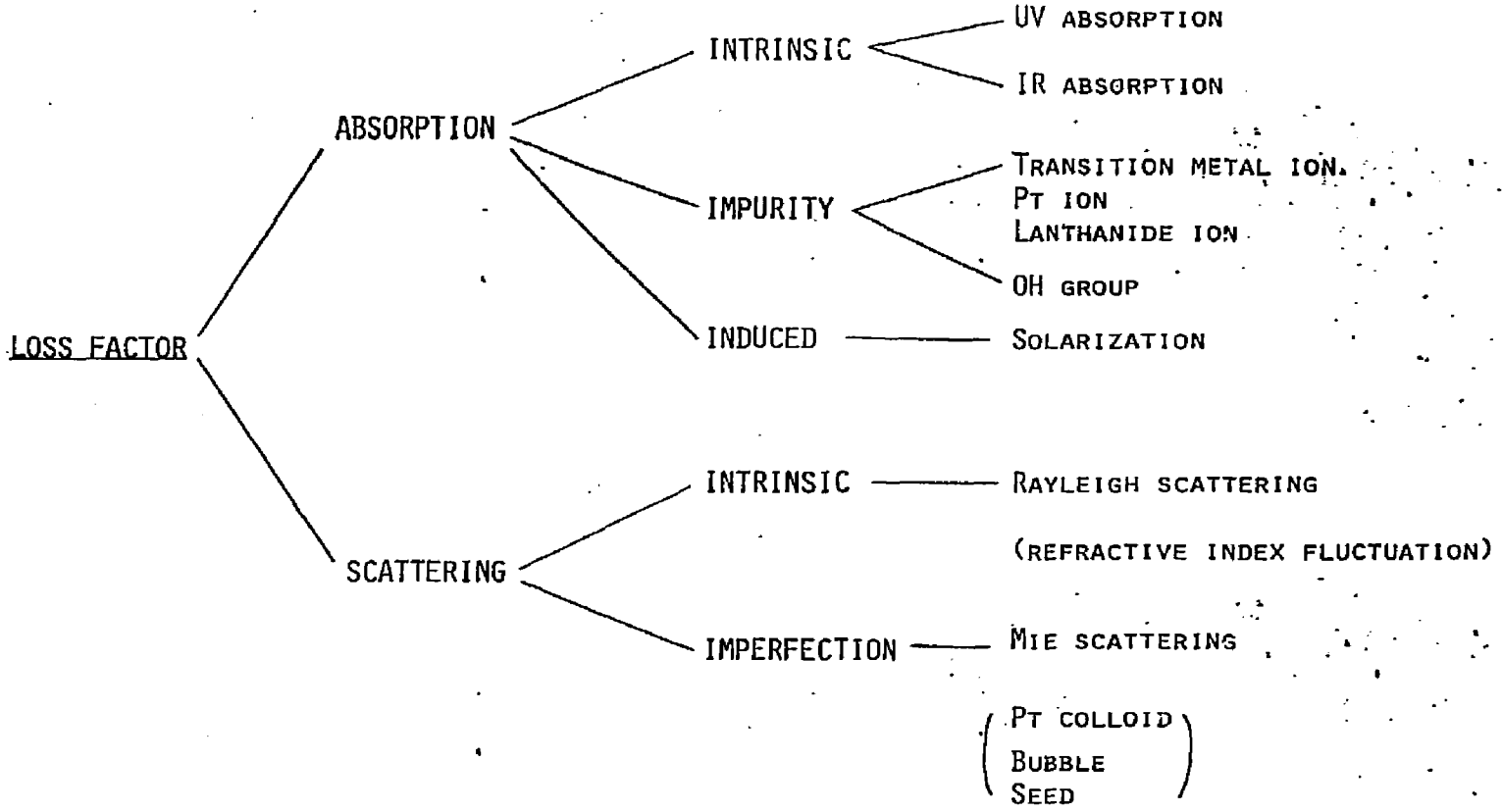
Sample No.	Parameter	Dehydration Condition	Pt Conc. (ppm)	Melting time (hrs)	Absorption			Loss @ 1.05 μ	
					@400nm ¹⁾ (cm ⁻¹)	@1.44 μ ¹⁾ (cm ⁻¹)	@3.35 μ (cm ⁻¹)	(10 ⁻⁴ cm ⁻¹) Predicted/Measured ¹⁾	
LL-12	OH content	Nothing	---	2	0.04	1.4	~30.0	<2.7	~3 ²⁾
11		O ₂	---	2	0.10	0.61	12.6	"	<3 ³⁾
10		specific gas	---	2	0.01	0.13	3.0	"	"
13		specific gas	---	2	0.01	0.05	2.0	"	"
LL-16	Pt concentration	specific gas	200	2	0.53	0.05	1.5	"	"
17		specific gas	500	2	0.89	0.05	2.0	"	"
LL-14	Contamination	specific gas	---	7	0.01	0.05	2.3	"	"
15		specific gas	---	17	0.01	0.05	1.4	"	"

1) Measured by LLNL

2) Obvious absorption around 1.0 μ due to OH

3) Weak trace of absorption around 1.0 μ due to OH

FIGURE 1



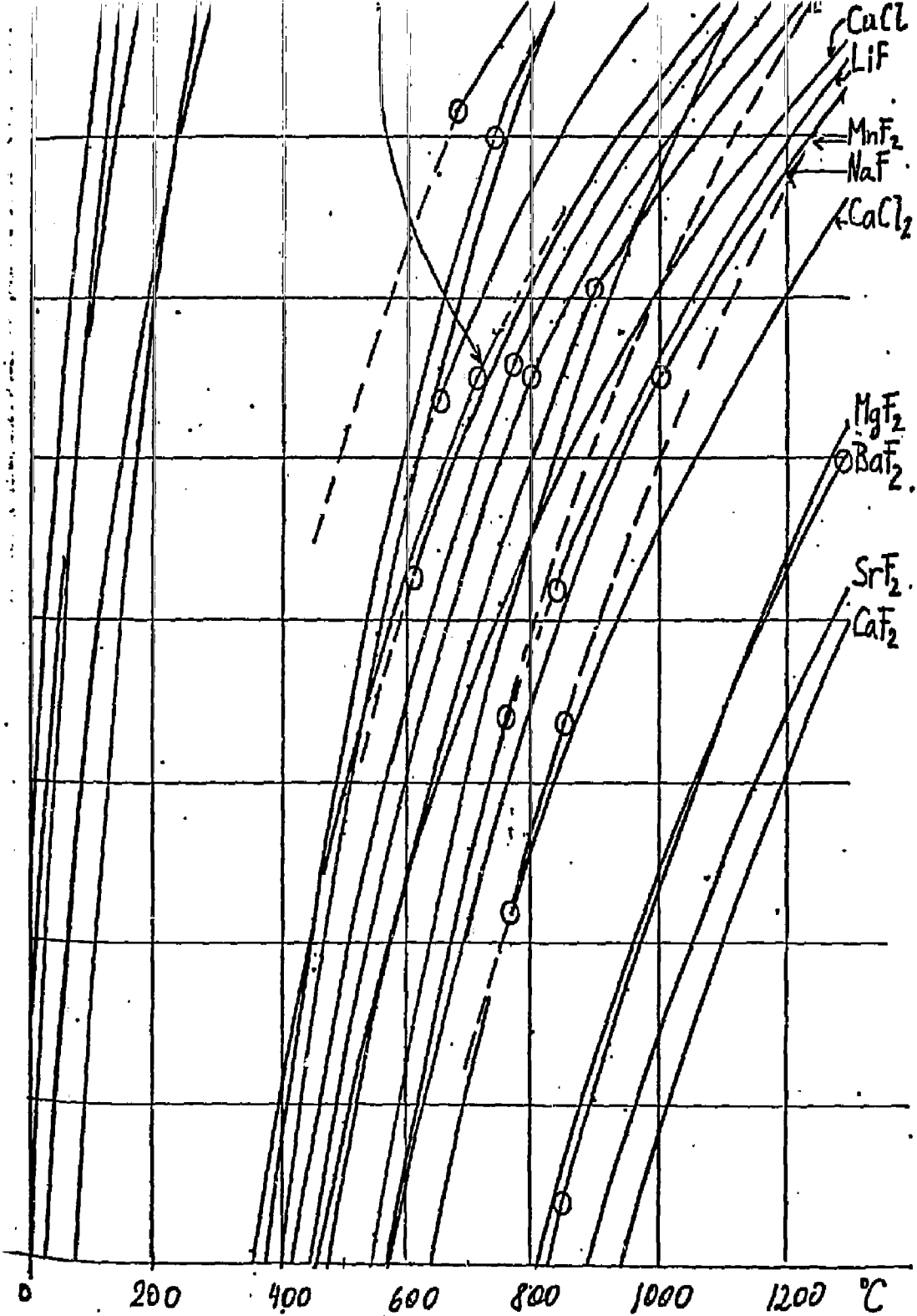


FIGURE 1. Vapor pressures of fluorides and chlorides of laser glass batch components and some transition metal impurities.

O melting points

Δ sublimation points

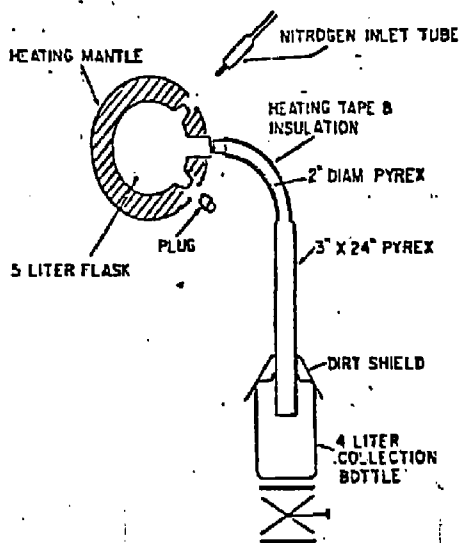
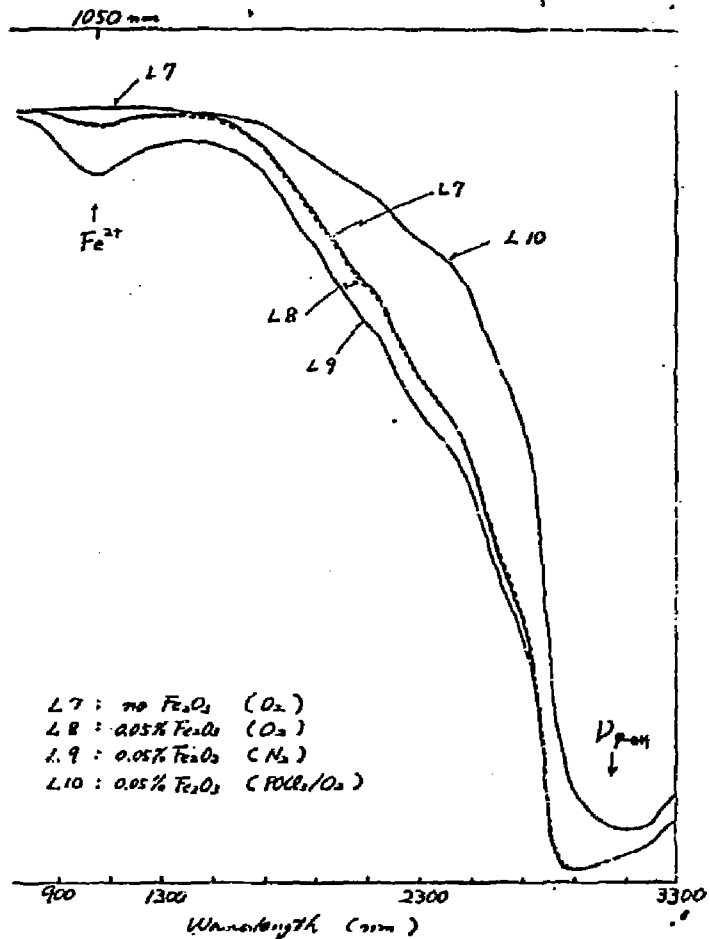
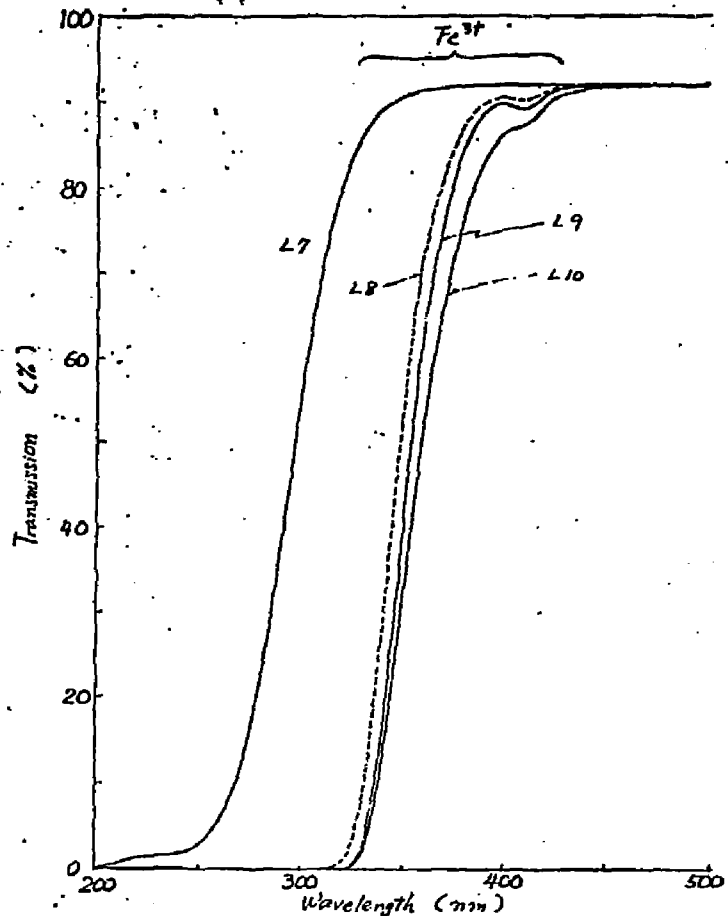


FIGURE 3 Sublimation equipment for P_2O_5



- L7 : no Fe_2O_3 (O_2)
- L8 : 0.05% Fe_2O_3 (O_2)
- L9 : 0.05% Fe_2O_3 (N_2)
- L10 : 0.05% Fe_2O_3 ($FOCl_2/O_2$)

Figure 4 Effect of melting condition to Fe^{3+}/Fe^{2+} ratio

Figure 5a

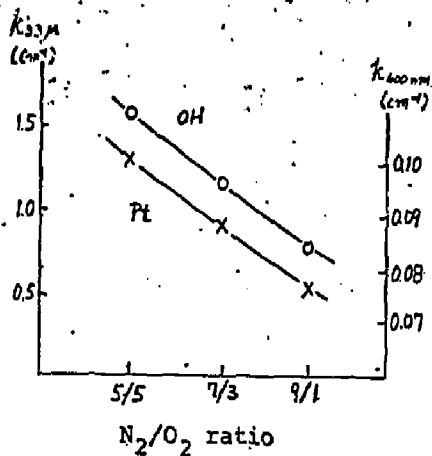


Figure 5b

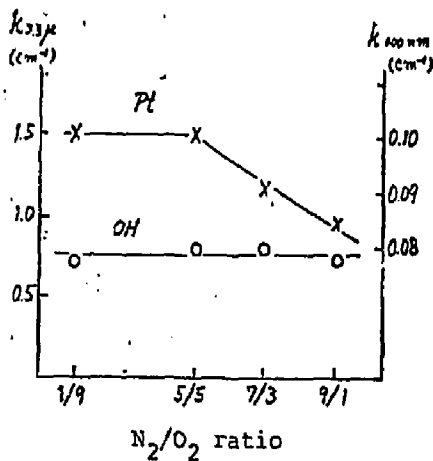


Figure 5c

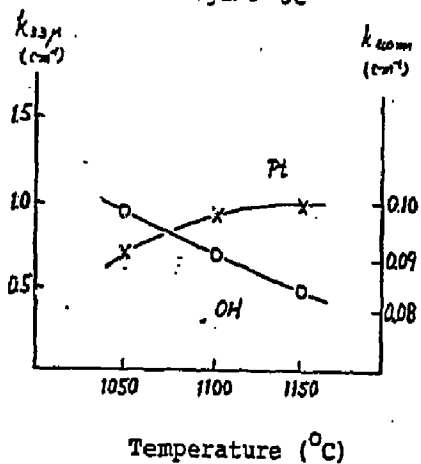
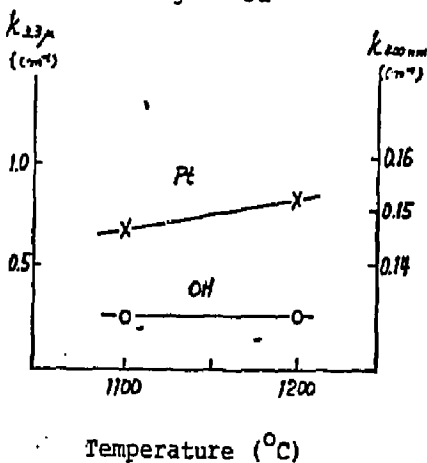


Figure 5d



- Fig. 5a Effect of carrier gas composition
 Fig. 5b Effect of atmosphere control gas composition
 Fig. 5c Effect of dehydration temperature
 Fig. 5d Effect of refining temperature

LL-12

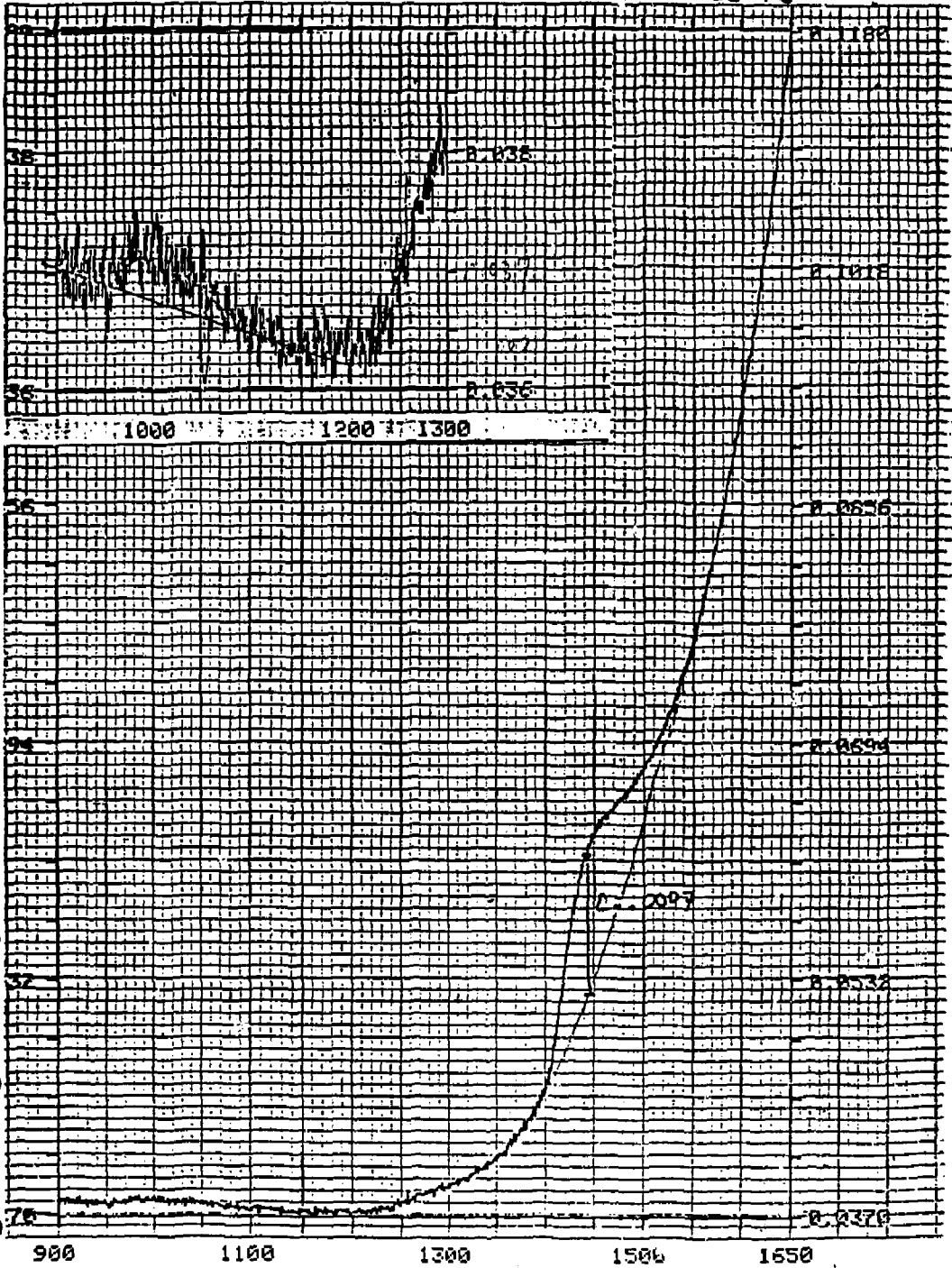


FIGURE 6 Absorption spectra of highly water containing glass