HOYA OPTICS U.S.A., Inc.

2200 Sand Hill Road, Suite 200, Menlo Park, CA 94025 PHONE (415) 854-4680 TELEX 345-539

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AN INVESTIGATION ON THE DAMAGE THRESHOLD OF FILMS
COATED ON VARIOUS SILICATE, FLUOROPHOSPHATE AND
PHOSPHATE LASER GLASSES

Final Report
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✓ Yuji Nakajima and Tetsuro Izumitani
Hoya Corporation
Tokyo, Japan

MASTER

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Abstract

Effects of substrate laser glass on the damage threshold and adhesion of dielectric films has been studied in order to improve the damage threshold. The study is divided into two Parts: the first Part dealing with four types of laser glass, LSG-91H silicate, LHG-8 phosphate, P-1 phosphate and LHG-10 fluorophosphate; the second Part dealing with twenty six glasses with systematically modified compositions in three glass systems, silicate, phosphate and fluorophosphate.

In Part I, It was found that the highest damage threshold was obtained with alkaline rich P-1 phosphate glass. Low damage threshold was found on LHG-10 fluorophosphate glass. When using LSG-91H silicate glass, the oxide films of Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 and Ta_2O_5 exhibited better adhesion and higher damage threshold than the fluoride films of MgF_2 , LaF_3 and CeF_3 . When using LHG-8 phosphate glass, the fluoride films exhibited better adhesion and higher damage threshold than the oxide films. There appears to be a correlation between laser damage threshold and adherence, that is, better adhesion gives higher damage threshold.

In Part II, It was found that an increase in network former and intermediate improved the adhesion of both SiO_2 film and MgF_2 film in all the glass systems except phosphate glass system. Network modifiers such as R^+ and R^{++} ions produced poorer adhesion with its larger ionic radius. Damage measurements for MgF_2 films on fluorophosphate glasses showed that addition of P_2O_5 content to replace AlF_3 lowered the damage threshold. The substitution of CaO content or SrO content for BaO content decreased the damage threshold. For MgF_2 , CeF_3 , SiO_2 and Ta_2O_5 films coated on phosphate glasses, an effect of glass compositions on the damage threshold remains obscure.

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1. INTRODUCTION

Although there have been investigations on the effect of glass surface texture on the laser induced damage in thin film, there is no reported work on the correlation of the film-glass affinity to thin film damage. It is generally known that this affinity is somewhat related to the film structure which in turn may have an effect on the film damage. Nakajima, Izumitani and Fukuoka¹⁾ studied the adhesion of chromium films on various glass substrates and have shown that the adhesion is profoundly influenced by glass compositions.

In the present report, effects of substrate glass on both the damage threshold and the adhesion of films have been studied. The study is divided into two Parts: the first Part dealing with three types of commercial laser glass, LSG-91H silicate, LHG-8 phosphate and LHG-10 fluorophosphate; the second Part dealing with twenty six glasses with systematically modified compositions in three glass systems, silicate, phosphate and fluorophosphate.

2. EXPERIMENTAL

2.1. Film preparation

Four types of laser glass, which are LSG-91H silicate, LHG-8 phosphate, alkaline rich P-1 phosphate and LHG-10 fluorophosphate glasses, were used as a substrate in Part I. The properties of these laser glasses are given in Table 1. Twenty six glasses in Part II were prepared with systematically modified compositions in three glass systems; silicate, phosphate and fluorophosphate. The compositions of these glasses are given in Tables 6, 7 and 8.

Glass specimen of 29 mm in diameter and of 8 mm in thickness were polished using Polytex polisher with CeO_2 polishing grains suspended in water (10%). They were cleaned in detergent solution, rinsed in flowing distilled water and degreased in iso-propyl alcohol and finally dried by Freon vapour.

The films of MgF_2 , LaF_3 , CeF_3 and ThF_4 were prepared using thermal evaporation at pressures of 3×10^{-5} torr to 10^{-6} torr.

The films of Al_2O_3 , SiO_2 , ZrO_2 , TiO_2 and Ta_2O_5 were evaporated using an electron beam gun at pressures below 10^{-4} torr. The deposition rate was $5 \pm 3 \text{ \AA/sec}$. The substrate temperature was $300 \pm 10^\circ\text{C}$. The optical thickness of films was $1.06/4 \text{ }\mu\text{m}$ for experiments in Part I and was $1.06/2 \text{ }\mu\text{m}$ for experiments in Part II.

2.2 Damage measurement

Laser damage thresholds were measured with 1 ns, $1.06 \text{ }\mu\text{m}$ laser pulses at Lawrence Livermore Laboratory for all films in Part I and for films evaporated onto phosphate glasses in Part II. Laser pulses of 3 ns, $1.06 \text{ }\mu\text{m}$ at Hoya Corporation were used for MgF_2 films evaporated onto fluorophosphate glasses in Part II.

2.3. Adhesion measurement

The adhesion was evaluated by scratch test which was developed by Heavens²⁾. Benjamin and Weaver³⁾ analyzed the scratch test in detail. They have proposed that film detachment is caused by the shear force at film/substrate interface around rim of the indentation produced by the stylus. It was also showed that simple relation between the applied load on the stylus and the shear force. Thus the adhesion could be calculated as a shear force F .

$$F = \frac{a P}{\sqrt{r^2 - a^2}}, \quad a = \sqrt{\frac{W}{\pi P}}$$

where

W: critical load.

r: radius of the stylus, 0.003 cm.

F: shear force per unit area due to deformation of the substrate.

a: radius of the circle of contact.

P: indentation hardness of the substrate (Knoop hardness used in the present work).

In the present work, a diamond scratch stylus with a tip radius of 0.003 cm was drawn across the film surface at the rate of 1 mm/sec by motorized drive. The vertical load was applied to the stylus and gradually increased until a critical load was reached at which the film was removed from the substrate. The critical load and the shear force are taken as a measure of the adhesion.

3. RESULTS AND CONCLUSIONS

3.1. Part I : DAMAGE THRESHOLD AND ADHESION OF VARIOUS DIELECTRIC FILMS ON LASER GLASSES: LSG-91H, LHG-8 and LHG-10

3.1.1. Adhesion

Table 2 shows critical load data of scratch test for various dielectric films on laser glasses: LSG-91H silicate, LHG-8 phosphate and LHG-10 fluorophosphate. Figure 1 also shows adhesion data in terms of shear force F . Using LSG-91H silicate glass as a substrate, more than 150 g critical load ($F = 19 \times 10^9 \text{ dyn cm}^{-2}$) was obtained for the oxide films of SiO_2 , Al_2O_3 , ZrO_2 , Ta_2O_5 and TiO_2 . The critical load for over 150 g was not determined, because LSG-91H silicate glass surface exhibits conchoidal fracturing over 150 g. For fluoride films of MgF_2 , LaF_3 and CeF_3 , the critical loads were in the low range of 5 to 20 g ($F = 3 \times 10^9 \sim 4 \times 10^9 \text{ dyn cm}^{-2}$). On the other hand, when LHG-8 phosphate glass and LHG-10 fluorophosphate glass were used as a substrate, the oxide films had a low critical load and the fluoride films exhibited a high critical load. The hardness of ThF_4 films was so low that its critical load could not be measured.

From these data, it can be conclude that LSG-91H silicate glass adhere well to the oxide films but poor to the fluoride films, whereas LHG-8 phosphate glass and LHG-10 fluorophosphate glass do not adhere well to the oxide films but adhere well to the fluoride films.

3.1.2. Damage Threshold

Figure 2 shows the laser damage thresholds of the dielectric films on the laser glasses. The observed points have an error of ± 1.2 to $\pm 0.4 \text{ J / cm}^2$, which is not indicated in this figure. The highest damage threshold was obtained by using alkaline rich P-1 phosphate glass with all films except TiO_2 film. LHG-10 fluorophosphate glass provided the lowest damage threshold except when LaF_3 , CeF_3 and ZrO_2 were used and exhibited the second lowest threshold. The films on LHG-8 and LSG-91H glasses exhibited

intermediate damage thresholds between P-1 glass and LHG-10 glass. Figure 3 provides a clearer comparison of the damage thresholds for LHG-8 glass and LSG-91H glass. Each rectangle in figure accounts for the damage threshold having an error of $\pm 1.1 \text{ J/cm}^2$ to ± 0.4 . It should be noted that when using LHG-8 phosphate glass the fluoride films gave a higher damage threshold than the oxide films except for SiO_2 film. On the other hand, with LSG-91H silicate glass, the oxide films exhibited a higher damage threshold than the fluoride films except for ThF_4 film. These results suggest that the laser damage threshold depends on the glass type.

3.1.3. Light Emission Threshold

Table 3 compares the light emission threshold to the damage threshold. For P-1 glass, with which the highest damage threshold was obtained, the difference was plus or zero. That is, the damage threshold was higher or roughly equal to the light emission threshold. The films on P-1 glass were not damaged prior to the light emission. For LHG-10 glass, with which a low damage threshold was observed, the difference was minus or zero. The films on LHG-10 glass were damaged before or at the same time as the light emission commenced. For LHG-8 glass, with which fluoride films had a higher damage threshold than oxide films except for MgF_2 and SiO_2 films, the difference was plus or zero for fluoride films, and minus for oxide films except for MgF_2 and SiO_2 films. For LSG-91H glass which exhibits a higher damage threshold with fluoride films compared to oxide films, minus differences resulted with fluoride films and plus or zero differences were obtained with oxide films except for SiO_2 film. The above results suggest that the difference between the damage threshold and the light emission threshold is a combination of both the film and the glass.

Figure 4 shows the relation between the damage threshold and the difference of the light emission threshold from the damage threshold. The damage threshold became higher as the difference increased.

3.1.4. Correlation between Adhesion and Damage Threshold

3.1.4-1. LHG-8 phosphate glass

Table 4 summarizes the results obtained with films on LHG-8 phosphate glass. The second column of the table illustrates the film adherence. The third indicates the difference between the damage threshold of LHG-8 glass and LSG-91H glass. The fourth column represents the difference between the damage threshold and the light emission threshold. The fluoride films evaporated on LHG-8 phosphate glass exhibited a good adhesion and a higher damage threshold than when LSG-91H glass was used, and, with the exception of MgF_2 film, the damage threshold was also higher or equal to the light emission threshold. On the other hand, the oxide films exhibited poor adhesion and a lower damage threshold than LSG-91H glass, and the damage threshold was lower than the light emission threshold.

Figure 5 shows the relationship between the damage threshold and the adhesion for the film on LHG-8 glass. The critical load at which the film was removed from the substrate by scratching denotes the film adhesion. It was found that the fluoride films exhibited a better adhesion and a higher damage threshold, whereas the oxide film showed a poorer adhesion and a lower damage threshold.

The above results suggest that the adhesion of films affects the damage threshold.

3.1.4-2. LSG-91H silicate glass

Table 5 summarizes the results of the films on LSG-91H glass. Unlike LHG-8 phosphate glass, the fluoride film had poor adhesion and a lower damage threshold than LHG-8 glass. The damage threshold was also lower than the light emission threshold. The oxide films exhibited good adhesion, had a higher damage threshold than LHG-8 glass, and the damage threshold was higher or equal to the light emission threshold except with SiO_2 film.

Figure 6 shows the relationship between the damage threshold and the adhesion of films on LSG-91H glass. The oxide films exhibited a better adhesion and a higher damage threshold, whereas the fluoride films showed a poorer adhesion and a lower damage threshold.

The above results indicate again that the film adhesion affects the damage threshold.

3.1.5. Summary for Part I

- 1) The highest damage threshold was obtained with alkaline rich P-1 phosphate glass.
- 2) Low damage threshold was found on LHG-10 fluorophosphate glass.
- 3) When using phosphate glass, the fluoride films exhibited better adhesion and higher damage threshold than the oxide films.
- 4) When using LSG-91H silicate glass, the oxide films exhibited better adhesion and higher damage threshold than the fluoride films.
- 5) There appears to be a correlation between laser damage threshold and adherence, that is, better adhesion gives higher damage threshold.

3.2 Part II : EFFECTS OF GLASS COMPOSITIONS ON DAMAGE THRESHOLD AND ADHESION

3.2.1. Damage Threshold

3.2.1-1. Fluorophosphate Glass

Effect of glass compositions on the damage threshold have been studied in twenty six glasses with systematically modified compositions in three glass systems; silicate, phosphate and fluorophosphate. The compositions of these glasses are given in Tables 6, 7 and 8.

Figure 7 shows effects of additional P_2O_5 to replace AlF_3 on the damage threshold for MgF_2 films. The damage threshold was improved with decrease in P_2O_5 from 40% cationic% to 20%. But further decrease of P_2O_5 from 20% to 15% lowered the threshold. Effects of AlF_3 and RF_2 on the damage threshold for MgF_2 film is shown in Fig.8. A decrease in AlF_3 appear to improve the damage threshold. In $RF_2(40\%)-PO_{2.5}(40)-AlF_3(20)$ system, the damage threshold was smaller in the order of BaF_2 rich glass, SrF_2 rich glass and CaF_2 rich glass (Fig.9). The substitution of NaF for RF_2 improved the threshold (Fig.9).

3.2.1-2. Phosphate Glass

Damage threshold was studied in glass composition shown in Figs.10, 11, 12 and 13. Films tested were MgF_2 , CeF_3 , SiO_2 or Ta_2O_5 as shown in each figure. Ta_2O_5 film always exhibited lower damage threshold than fluoride films of MgF_2 and CeF_3 . This results agree with those obtained in 3.1.2. It seems that there is no clear correlation between glass compositions and the damage threshold.

3.2.2. Adhesion

3.2.2-1. Silicate Glass

Figures 14a,14b,14c and 14d show the shear force for MgF_2 and SiO_2 films on silicate glasses. The adhesion changed with modified compositions in glass. It was found that:

a) Addition of SiO_2 to replace Na_2O improved the adhesion(Fig.14a).

- b) Addition of Al_2O_3 to replace BaO also improved the adhesion (Fig. 14b).
- c) In $\text{R}_2\text{O}(15 \text{ mol}\%)-\text{SiO}_2(65)-\text{BaO}(20)$ system, the adhesion became poorer in the order of Li_2O , Na_2O , K_2O used as R_2O (Fig.14c).
- d) In $\text{RO}(20 \text{ mol}\%)-\text{SiO}_2(65)-\text{Na}_2\text{O}(15)$ system, the adhesion strength decreased in the order of MgO , CaO , SrO , BaO used as RO (Fig.14d).

In these glass systems, the adhesion strength decreased as ionic radius of R^+ , R^{++} ions became larger. It was also shown that SiO_2 films always exhibited better adhesion than MgF_2 films in silicate glasses.

3.2.2-2. Phosphate Glass

Figures 15a, 15b, 15c and 15d show the shear force for MgF_2 and SiO_2 films on phosphate glasses. It was found that:

- a) SiO_2 films always exhibited poorer adhesion than MgF_2 films.
- b) Addition of P_2O_5 to replace Na_2O caused poor adhesion in SiO_2 films but no improvement on the adhesion of MgF_2 films (Fig. 15a).
- c) Addition of Al_2O_3 to replace CaO improved the adhesion (Fig. 15b).
- d) In $\text{R}_2\text{O}(30 \text{ mol}\%)-\text{P}_2\text{O}_5(55)-\text{Al}_2\text{O}_3(5)-\text{CaO}(10)$ system, the adhesion became poorer in the order of Li_2O , Na_2O , K_2O used as R_2O (Fig.15c).
- e) In $\text{RO}(10 \text{ mol}\%)-\text{P}_2\text{O}_5(55)-\text{Al}_2\text{O}_3(5)-\text{Na}_2\text{O}(30)$ system, the adhesion became poorer in the order of MgO , CaO , SrO , BaO used as RO (Fig. 15d).

3.2.2-3. Fluorophosphate Glass

Figures 16a, 16b and 16c show the shear force for MgF_2 and SiO_2 films on fluorophosphate glasses. It was found that:

- a) SiO_2 films always exhibited poorer adhesion than MgF_2 films.
- b) Addition of P_2O_5 to replace AlF_3 improved the adhesion (Fig.16a). Especially, a drastic change in adhesion was observed when P_2O_5 content increased from 15 cationic% to 20%. The structure of glass seems to change drastically in this range.
- c) Addition of AlF_3 to replace to RF_2 did not improved the adhesion (Fig. 16b).

- d) In $\text{RF}_2(40\%)-\text{PO}_{2.5}(40)-\text{AlF}_3(20)$ system, the adhesion became poorer in the order of CaF_2 , SrF_2 and BaF_2 used as RF_2 (Fig.16c).
- e) The substitution of NaF for RF_2 produced poor adhesion (Fig.16c).

3.2.3. Discussion and Conclusion for Part II

Adhesion of MgF_2 film and SiO_2 film in various glass compositions are summarized in Table 9 and as follows.

1) Network formar(NWF) / network modifier(NWM) ratio:

In silicate glass, increase of SiO_2 improved the adhesion. In phosphate glass, addition of P_2O_5 caused poor adhesion for SiO_2 films but no improvement on the adhesion of MgF_2 films.

2) NWF / intermediate oxide ratio:

In fluorophosphate glass, addition of P_2O_5 improved the adhesion.

3) Intermediate oxide / NWM ratio:

Increase in intermediate oxide improved the adhesion in silicate glass system and phosphate glass system.

4) Network modifier:

In all the glass systems, the adhesion strength decreased with larger ionic radius of modifier ions.

The damage threshold with respect to glass compositions are summarized as follows.

5) Fluorophosphate glass system:

5-1) Addition of P_2O_5 content (NWF) from 20 cationic% to 40 % lowered the damage threshold. But addition of P_2O_5 from 15 % to 20 % improved the threshold.

5-2) Addition of AlF_3 (intermediate) appear to lower the damage threshold.

5-3) The damage threshold became higher with larger ionic radius of modifier ions.

6) Phosphate glass system:

There is no clear correlation between glass compositions and the damage threshold.

The results described above suggest that there is no correlation between laser damage threshold and film adhesion, and they contradicts the conclusion in Part I which indicated that better adhesion gives higher damage threshold. This inconsistency may be reconciled, assuming that there are many factors affecting the damage threshold and that other factors except adhesion is dominant in the Part II. More detailed studies of glass compositions to the damage threshold will also be necessary.

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	LSG-91H [silicate]	LGH-8 [phosphate]	P-1 [phosphate]	LHG-10 [fluoro- phosphate]
Nd ₂ O ₃ (wt%)	3.1	3.03	0	2.302
Nd ³⁺ conc. (10 ²⁰ ions/cm ³)	3.04	3.074	0	3.001
Cross section for stimulated emission (10 ⁻²⁰ cm ²)	2.7	4.2	-	2.7
Life time (μsec)	300	315	-	401
Fluorescence half-line width (Å)	252	201	-	241
Center lasing wavelength (μ)	1.062	1.054	-	1.051
n ₂ (10 ⁻¹³ esu)	1.43	1.02	1.03	0.576
n _d	1.56115	1.52962	1.50759	1.45919
Yield point (°C)	505	520	392	459
Transformation point (°C)	465	485	359	435
Thermal expansion coeff. (10 ⁻⁷ /°C)	105	127	152	158
D _w (H ₂ O 100 l hr.) (wt.% loss)	0.036	0.13	2.116	0.05
Density (g/cm ³)	2.81	2.83	2.57	3.641
Knoop hardness (Kg/mm ²)	590	321	-	355

Table 1. Properties of laser glasses under test.

Film...	Critical Load (g)		
	LSG-91H	LHG-8	LHG-10
MgF ₂	5 ~ 20	> 150	> 50
LaF ₃	5 ~ 10	> 150	> 50
CeF ₃	5 ~ 10	> 150	> 50
SiO ₂	> 150	60	5
Al ₂ O ₃	> 150	50 ~ 70	5 ~ 20
ZrO ₂	> 150	70 ~ 90	5 ~ 20
Ta ₂ O ₅	> 150	80 ~ 100	30 ~ 40
TiO ₂	> 150	70 ~ 90	5 ~ 20

Table 2. Adhesion of various dielectric films to LSG-91H, LHG-8 and LHG-10 glasses.

Fig. 1 Film adhesion for various dielectric films on laser glasses; LSG-91H silicate, LHG-8 phosphate and LHG-10 fluorophosphate.

Fig. 2. Damage threshold of dielectric films evaporated on the laser glasses, which are P1 phosphate, LG-8 phosphate, LG-91H silicate and LG-10 fluorophosphate glasses.

Fig. 3 Damage threshold of dielectric films evaporated on LSG-91H silicate glass and LHG-8 phosphate glass.

Film Material	[Damage threshold] - [Light emission threshold] (J / cm ²)			
	LSG-91H	LHG-8	P-1	LHG-10
MgF ₂	≥ -2.7	< -2.9	> +1.8	≤ -2.1
SiO ₂	-1.7	> +0.8	> +3.0	< -1.1
ThF ₄	-2.1	0	> +2.4	-1.2
LaF ₃	-2.5	0		< -1.6
CeF ₃	< -2.5	+0.7	0	< -1.5
Al ₂ O ₃	0	< -2.5	0	< 0
ZrO ₂	+1.1	-1.4	> +0.2	0
Ta ₂ O ₅	0	-2.1		0
TiO ₂	> +1.9	< -1.1	0	< -1.7

Table 3. The difference between the damage threshold and the light emission threshold for various dielectric films on LSG-91H, LHG-8, P-1 and LHG-10 glasses.

Fig. 4. Damage threshold D_{th} versus the difference of light emission threshold from damage threshold $D_{th} - L_{th}$ for dielectric films on the laser glasses, P1, LHG-8, LSG-91H and LHG-10.

FILMS EVAPORATED ON LHG-8 GLASS

FILM MATERIAL	ADHESION	$D_{TH} - D_{TH}$ LHG-8 LSG-91H	$D_{TH} - L_{TH}$
MgF ₂	GOOD	+ 0.3	< - 2.9
LaF ₃	"	+ 1.8	0
CeF ₃	"	+ 3.2	+ 0.7
SiO ₂	POOR	+ 1.6	> + 0.8
Al ₂ O ₃	"	< - 0.6	< - 2.5
ZrO ₂	"	- 1.1	- 1.4
Ta ₂ O ₅	"	- 1.9	- 2.1
TiO ₂	"	- 1.4	< - 1.1

Table 4 Film adhesion, the difference in damage threshold between LHG-8 glass and LSG-91H glass, and the difference of damage threshold from light emission threshold for dielectric films on LHG-8 phosphate glass.

Fig. 5. Damage threshold versus critical load for the films on LHG-8 phosphate glass.

FILMS EVAPORATED ON LSG-91H GLASS

FILM MATERIAL	ADHESION	$D_{TH} - D_{TH}$ LSG-91H LHG-8	$D_{TH} - L_{TH}$
MgF ₂	POOR	- 0.3	≥ - 2.7
LaF ₃	"	- 1.8	- 2.5
CeF ₃	"	- 3.2	< - 2.5
SiO ₂	GOOD	- 1.6	- 1.7
Al ₂ O ₃	"	> + 0.6	0
ZrO ₂	"	+ 1.1	+ 1.1
Ta ₂ O ₅	"	+ 1.9	0
TiO ₂	"	+ 1.4	+ 1.9

Table 5 Film adhesion, the difference in damage threshold between LSG-91H glass and LHG-8 glass, and the difference of damage threshold from light emission threshold for films on LSG-91H silicate glass.

Fig. 6. Damage threshold versus critical load for the films on LSG-91H silicate glass.

SiO ₂	65	75	65	65	65	65	65	65	65	65
Al ₂ O ₃			0	5						
Li ₂ O					15					
Na ₂ O	35	25	15	15		15		15	15	15
K ₂ O							15			
MgO								20		
CaO									20	
SrO										20
BaO			20	15	20	20	20			20
Remarks	SiO ₂ /Na ₂ O effect		Al ₂ O ₃ /BaO		R ₂ O effect			RO effect		

Table 6. Compositions of silicate glasses (mol%)

P ₂ O ₅	50	55	65	55	55	55	55	55	55	55	55	55
Al ₂ O ₃	5	5	5	5	10	5	5	5	5	5	5	5
Li ₂ O						30						
Na ₂ O	35	30	20	30	30		30			30	30	30
K ₂ O								30				
MgO									10			
CaO	10	10	10	10	5					10		
SrO											10	
BaO												10
Remarks	P ₂ O ₅ /Na ₂ O effect			Al ₂ O ₃ /CaO		R ₂ O effect			RO effect			

Table 7. Compositions of phosphate glass (mol%).

PO _{2.5}	15	20	30	40	20	20	40	40	40	40
AlF ₃	35	30	25	20	30	35	20	20	20	20
NaF							40			
CaF ₂	30	30	27	24	30	27		24	8	8
SrF ₂	10	10	9	8	10	9		8	24	8
BaF ₂	10	10	9	8	10	9		8	8	24
Remarks	PO _{2.5} / AlF ₃ effect				Al ₂ O ₃ / RF ₂		RF	RF ₂ effect		

Table 8. Compositions of fluorophosphate glass.
(cationic %)

Fig. 7 Effects of additional P₂O₅ to AlF₃ on damage threshold for MgF₂ film.

Fig.8 Effects of AlF₃ to RF₂ on damage threshold for MgF₂ film.

Fig.9 Effects of RF₂ and RF on the damage threshold for MgF₂ film.

Fig.10 Effects of P_2O_5 and Na_2O on the damage threshold.

Fig.11 Effects of Al_2O_3 and CaO on the damage threshold.

Fig.12 Effects of R_2O on the damage threshold.

Fig.13 Effects of RO on the damage threshold.

Fig. 14a SiO₂/Na₂O effect

Fig. 14b Al₂O₃/BaO effect

Fig. 14c R₂O effect

Fig. 14d RO effect

more SiO₂ content: better adhesion more Al₂O₃ content: better adhesion larger ionic radius of R⁺: poorer adhesion larger ionic radius of R⁺⁺: poorer adhesion

Fig. 15a P₂O₅/Na₂O effect

more P₂O₅ content
poorer adhesion for SiO₂
no change for MgF₂ Film

Fig. 15b Al₂O₃/CaO effect

more Al₂O₃ content
better adhesion

Fig. 15c R₂O effect

larger ionic radius of R⁺
poorer adhesion

Fig. 15d RO effect

larger ionic radius of R⁺
poorer adhesion

Fig.16a $\text{PO}_{2.5}/\text{AlF}_3$ effect
more P_2O_5 content
better adhesion

Fig.16b $\text{Al}_2\text{O}_3/\text{RF}_2$
more Al_2O_3
no change

Fig.16c RF_2 and RF_2/RF effect
larger ionic radius of R^{++} change RF_2 for RF
poorer adhesion poorer adhesion

	NWF/NWM ratio		NWF/ITM ratio	ITM/NWM ratio	NWM effect	
	SiO ₂ /Na ₂ O →increase	P ₂ O ₅ /Na ₂ O →increase	P ₂ O ₅ /AlF ₃ →increase	Al ₂ O ₃ /RO AlF ₃ /RF ₂ →increase	radius of R ⁺ → larger	radius of R ⁺⁺ →larger
silicate glass	better adhesion			better adhesion	poorer adhesion	poorer adhesion
phosphate glass		poorer for SiO ₂ film no change for MgF ₂ film		better adhesion	poorer adhesion	poorer adhesion
fluoro- phosphate glass			better adhesion	no change	poorer adhesion	poorer adhesion

Table 9. The relationship between film adhesion and glass compositions for silicate glass system, phosphate glass system and fluorophosphate glass system.

NWF: network former. NWM: network modifier. ITM: intermediate.