HOYA OPTICS, INC.

MAIN OFFICE:

3400 Edison Way, Fremont, CA 94538-6138 (415) 490-1880 Telex: 172-647

EAST COAST OFFICE:

P.O. Box 246, Southbridge, MA 01550-0246 (617) 764-6604

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PRINCIPAL INVESTIGATOR

DR. T. IZUMITANI

INVESTIGATORS

H. TORATANI

T. MATSUKAWA

C. KANAMORI

H. MIYADE

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1. INTRODUCTION

Requirements for Zeus laser glass and HAP laser glass were small σ , low water, low concentration quenching and high mechanical and thermal strength in the former and high σ , low water, low concentration quenching and high mechanical, thermal shock resistance in the later.

In order to get a high mechanical and thermal shock resistance, we introduced SiO_2 into phosphate glass, because SiO_2 gives a low expansion coefficient.

2. CHEMICAL DURABILITY IN SILICO-PHOSPHATE GLASS

However, we were afraid whether two network former P_2O_5 component and SiO_2 component are compatible with each other. So, we started from P_2O_5 - SiO_2 two component system (Report No. 1). As we anticipated, we could get low expansion and high strength glass (Figure 2, Report No. 1) but chemical durability became worse with increasing SiO_2 content (Figure 7, Report No. 1). However, we found out that the weak chemical durability was improved completely by adding Al_2O_3 (Report No. 2, Figure 5; Report No. 3, Figure 2A).

Why such a phenomena occurs? It is assumed as follows:

As derived from IR spectra, the phosphate network is depolymerised by SiO_2 so that the SiO_2 rich phosphate glass consists of small number of molecules of PO_4 tetrahedra and SiO_4 tetrahedra network. Small molecules of PO_4 will be combined by OH radical and

molecule, for example, will be

easily dissolved into water. When Al_2O_3 is added, Al^{3+} ion will combine with PO_4 tetrahedra ion and inhibit the combination of OH radical to PO_4 tetrahedra, and thus the dissolution of PO_4 tetrahedra will be prevented.

3. HIGH WATER CONTENT AND HIGH EVAPORATION TENDENCY IN HIGH SiO₂ CONTENT SILICOPHOSPHATE GLASS

There were the other two problems in silicophosphate glasses. One is hygroscopic property and the other is high evaporation tendency. It was found out that there are two regions with different properties in P₂O₅-SiO₂-Li₂O system (Report No. 6, Figure 1B). One is high Li₂O content region (A region) which has low water content and low evaporation tendency. The other is high SiO₂ content region (B region) which has high water content and high evaporation tendency.

High hygroscopic property and high evaporation tendency come from the same cause as weak chemical durability. As mentioned above, high SiO₂ content silicophosphate glass (B type) consists of small molecules of PO₄ and SiO₄ network (Report No. 8, Figure 9). OH radicals easily combine with PO₄ tetrahedra and forms

molecules which evaporate easily.

The dissolved water in both (A and B) regions of P₂O₅-SiO₂-Li₂O system was removed by PCl₃ gas bubbling as shown in Figure 5B, Report No. 3. The high evaporation tendency was improved very much with the addition of Al₂O₃ (Report No. 6, Figure 1A). The reason is the same as in chemical durability. However, the glasses in region A with high Li₂O content have low evaporation tendency.

4. LASING PROPERTIES OF SILICOPHOSPHATE GLASSES

- a. Cross section for stimulated emission (σ) in P₂O₅-SiO₂-Li₂O system is mainly determined with P₂O₅ content (Report No. 6, Figure 3A). Asymmetry around Nd³⁺ ion in the chain structure of phosphate glass gives higher cross section (TORATANI & IZUMITANI: J. Non-Cryst. Solid 47 (1) 87 (1982)). But we could not understand clearly the reason why higher SiO₂ content glasses have a little bit higher cross section than higher Li₂O content glasses.

- b. The fluorescence life time of silicophosphate glass is strongly affected by water content. The relationship between glass composition and life time of water free glasses is shown in Report No. 6, Figure 4. Life time becomes shorter with P_2O_5 content and lower with Li_2O content which is similar to cross section tendency. One of the reasons for longer life time in high Li_2O content glass is due to low non-radiative decay rate of high modifier content glass (Ibid, Non-Cryst. Solid 47 (1) 87 1980).
- c. Concentration quenching behavior of silicophosphate glass according to Russian book, ultraphosphate glass shows lower concentration quenching. It is clearly seen from Report No. 3, Figure 7 that high P_2O_5 content glasses have lower concentration quenching tendency than high SiO_2 content glasses. Ultraphosphate glass with P_2O_5 content 50 - 60 mol % shows longer life time. No. 8 and No. 11 glass in region A with SiO_2 content less than 25 mol % are most suitable from the view point of concentration quenching behavior (Report No. 3, Figure 7).

5. MECHANICAL AND THERMO-MECHANICAL PROPERTIES OF SILICOPHOSPHATE GLASS

As we expected, SiO_2 gives lower expansion coefficient (Report No. 4, Figure 1), higher toughness strength K_{IC} (Report No. 4, Figure 2). And it gives higher thermal conductivity than P_2O_5 component. As a result, SiO_2 gives higher thermal shock resistance R' (Report No. 4, Figure 5).

6. EFFECT OF Al_2O_3 ON SILICOPHOSPHATE GLASS

In order to improve the chemical durability and evaporation tendency, Al_2O_3 should be added to silicophosphate glass. The effect of Al_2O_3 on P_2O_5 - SiO_2 - Li_2O system was reported in Reports No. 5 and 6. Replacement of SiO_2 with 5% - 10% Al_2O_3 reduced σ . Life time increased with 5% Al_2O_3 but a

little bit decreased with 10% Al_2O_3 . Young's modulus and toughness increased with Al_2O_3 . Thermal expansion coefficient a little bit decreased with SiO_2 - Al_2O_3 exchange. It was found that SiO_2 gives higher thermal conductivity than Al_2O_3 but thermal shock resistance increased with 10% SiO_2 - Al_2O_3 exchange.

Therefore, it is concluded that higher SiO_2 content, higher Al_2O_3 content glass composition give higher thermal shock resistance.

7. EFFECT OF ALKALI AND ALKALI EARTH IONS ON SILICOPHOSPHATE GLASS

The effects of R_2O and RO components on the properties of silicophosphate was examined in the 7th Report.

As shown in Table 1 and 2 in Report No. 7, σ increased with ionic radius of cations and decreased with increase of valency. τ decreased with increase of valency and chemical durability, thermal expansion, mechanical strength and thermal resistance is determined by cationic field strength Z/a^2 , ie, chemical durability became better, α becomes smaller, K_{IC} becomes higher and R becomes higher.

8. GLASS COMPOSITION OF ZEUS GLASS AND HAP GLASS

Glass compositions of Zeus glass and HAP glass were selected from region A. Because the glasses with high SiO_2 content in region B showed low chemical durability, high water content, high evaporation tendency and high concentration quenching tendency. In region A, higher SiO_2 content glass was chosen because SiO_2 gives higher toughness and higher thermal shock resistance. For the Zeus glass containing maximum Nd_2O_3 concentration of 5 wt. %, 10% Al_2O_3 was introduced in order to get small σ . Thus Z35 and Z115 glass composition were decided as Zeus glass candidates (Report No. 7).

Regarding to HAP glass containing maximum Nd_2O_3 content of 10 wt. %, 5% Al_2O_3 was introduced in order to get higher σ . Thus H310 glass composition was decided as HAP glass candidate (Report No. 8).

Table below shows properties of Z115 and H310:

	σ	τ		D_w	R' ratio to LHG-5
Z35	$3.59 \times 10^{-2} \text{cm}$	292	sec (2 mol% Nd_2O_3)	0.09	1.74
Z115	3.30	295		0.10	1.48
H310	3.88	198	(4 mol% Nd_2O_3)	0.27	1.62

9. GLASS STRUCTURE OF REGION A AND B SILICOPHOSPHATE GLASS

The IR reflection spectra showed that No. 3 glass in region B consists of P_2O_5 and SiO_2 network while No. 8 and 11 glasses in region A consist of P_2O_5 chain structure (Report No. 8, Figure 7).

In region A, Al^{3+} (coordination no. 6) exist as modifier ions as well as Nd^{3+} and Li^+ as shown in Report No. 8, Figure 6. Si^{4+} also exists as modifier ions (coordination no. 6) as well as Al^{3+} as seen in Report No. 8, Figure 8.

Thus, the structures of glasses in region A and B are shown schematically in Report No. 8, Figure 9.

10. SUMMARY AND CONCLUSION

Investigation on silicophosphate glass is summarized as follows:

- A. There are two regions in silicophosphate glass. Glasses in region A are essentially phosphate glass and have strong chemical durability, low water content and low evaporation tendency, and give good laser glass, while the glasses in region B have reverse poor properties and are not suitable as laser glass.

- B. Water in phosphate glass is removed by PCl_3 gas bubbling.
- C. Chemical durability is completely improved by addition of Al_2O_3 .
- D. Evaporation tendency is suppressed by choosing glasses in region A and adding of Al_2O_3 .
- E. In order to get high mechanical strength, SiO_2 content should be increased but is limited because fluorescent life time become shorter by concentration quenching.
- F. About 60% P_2O_5 content gives suitable σ values and long life time.
- G. σ value is controlled by the content of P_2O_5 and Al_2O_3 .

Thus, we concluded from the investigation of Z35 and H310 as Zeus glass and HAP glass which almost satisfy the requirements for the laser glass in Zeus system and HAP system.