Durable Phosphate Glasses with Low Glass Transition Temperatures

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1.0 Abstract

Phosphate glasses have special applications, but traditionally never have had both durability and a low glass transition temperature (making them hard to work with). A composition study was used to find a more durable, easily fabricated phosphate glass with a low glass transition temperature. Batching, melting, casting, annealing and fabrication of test parts were performed. Glasses were characterized for hardness, glass transition temperature and chemical durability. An interesting composition with small amounts of borate, tin and alumina was found to have improved durability with a low glass transition temperature. Future work could include further composition improvement and doping with rare earth ions to study their electro-optical effects in the glass.

2.0 Background and Objectives

In the past, phosphate glasses have seldom incorporated durability with a low transition temperature. It would be beneficial to achieve the production of a glass with both of these characteristics because it would allow for molded phosphate optics and could possibly be a durable Nd^{+3} or Tb^{+3} host. Durability in water is the main issue because most optics are left in air where they are open to attack by water vapor. A Chinese group was able to produce a phosphate glass with both of these properties. They published a paper in the American Ceramic Society Bulletin with their findings.[1] The ingredients were given in the paper but the exact compositions were not. The initial goal of the experiment was to reproduce and possibly improve upon their compositions, but because accurate comparison was difficult other standards for comparison were chosen. A phosphate laser glass, LHG-8, was chosen as a standard because it has relatively good durability for a phosphate glass[2], but it has a high glass transition temperature, T_g. A phosphate glass, which we designate as "443"[3], developed for use in an optical fabrication course at the University of Rochester was chosen as another standard. It exhibits relatively poor durability in water, but it has a low T_g. The objective of this experiment was to create a glass with a mixture of the favorable characteristics of LHG-8 and 443 which could later be doped with rare-earth ions to give the glass electro-optical properties.

3.0 Initial Work

An initial composition based on information the Chinese released about their most durable glass was devised in the USA. It assumed any unknown quantities in the composition to be equal. It was melted using the chemical precursors identified in reference 1. The use of three carbonates resulted in excessive bubbling and boiling over of the melt (which could potentially harm the melting furnace). Another trial was completed in which the calcium carbonate and zinc carbonate were replaced with calcium oxide and zinc oxide. Excess bubbling was still observed. However a glass was formed which was then ground, polished and tested for hardness. The fact that a glass (which could be polished and tested) was formed made further experimentation seem feasible.

4.0 Manufacturing

4.1 Melting and Annealing

All components were weighed on a balance that provided measurements accurate to $\pm$ 0.01g. Components were mixed in 100 g batches with a mortar and pestle. Melting then was carried out in large ceramic crucibles.[4] Glasses were melted at $1000^{\circ}C$ for 90 minutes, with hand stirring 40 minutes into the processes. Problems with volatilization arose and an alternate melting schedule was devised. This involved ramping the temperature up to $1000^{\circ}C$ over 150 minutes, followed by the 90-minute melting period at $1000^{\circ}C$. Glasses were poured into graphite molds,[5] which had been pre-heated to $450^{\circ}C$. The annealing schedule in these molds consisted of 30 minutes at $450^{\circ}C$, followed by a $0.5^{\circ}C$ per minute ramp down to $300^{\circ}C$, after which the annealing oven was turned off. After approximately 18 hours the blocks of glass were shaken out of the molds, and were ready for finishing.
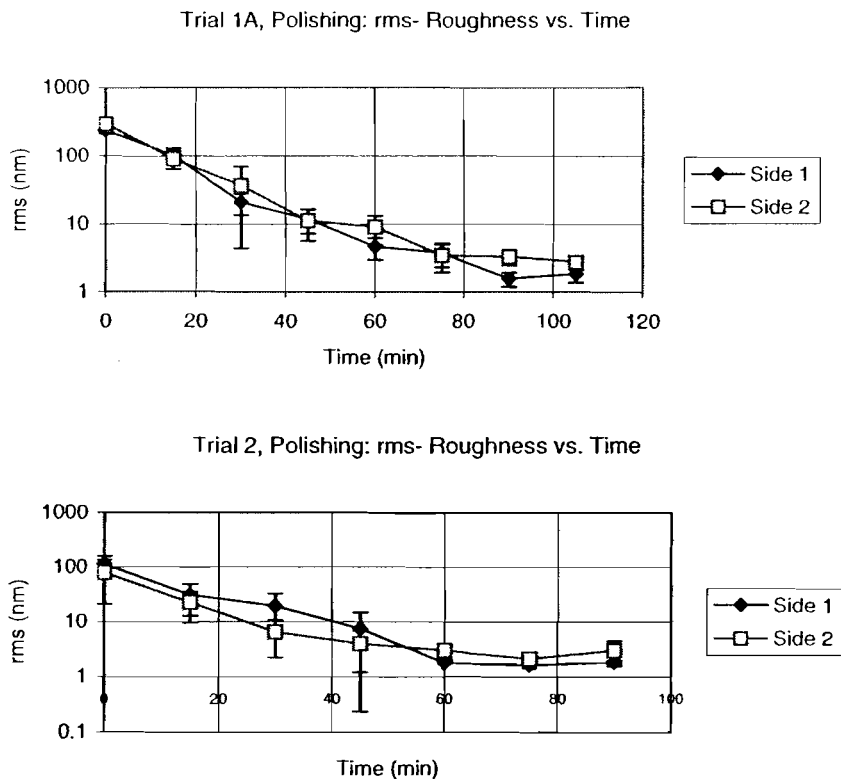
4.2 Finishing

The glass blocks taken from the molds were first ground to size (approximately 26mm x 26mm x 12mm). Grinding was done using 3M Trizact™ Film, color-coded, aluminum oxide pads.[6] These pads were mounted on flat, cast iron tools and placed on a single spindle grinding machine, rotating counterclockwise. These pads were flooded with tap water using a hand held squirt bottle. Each part was placed on the pad and moved with moderate hand pressure clockwise by hand in an oval shaped path. Grinding was done in three steps based on the three, color-coded pads. The green pads were the coarsest and were used first. Each part was ground with the green pads until all shine and texture was removed, and they were within $\pm$ 2mm of the desired size. This involved removing between 1mm and 3mm from each side. Bevels were also added to all sides at this stage. The blue pads were used for a medium grind. Each part was ground on them for one to two minutes on each side, and about 30 seconds on each beveled edge. The orange pads were the finest and the last used. Each part was ground on them for two to three minutes

per side, and 30 seconds on each beveled edge. Fine grinding resulted in about a 200 nm rms surface roughness on all ground surfaces.

Following grinding, each part was polished on the two opposing 26mm x 26mm faces using the white 3M Trizact™ Film polishing pads which contained bound cerium oxide. Polishing was done on a single spindle-polishing machine, rotating counter-clockwise at approximately 150 rpm. The hand polishing procedure was the same as the grinding procedure with the exception that a pump was used to keep the pad wet with DI water, which was added at a rate of 50 ml/min. For Trials 1A and 2 (see section 6.0), surface roughness measurements were taken after every 15 minutes of polishing to get an idea of the polishability of these glasses. Measurements were made on a Zygo New View™ 5000® white light interferometer, with a 20x objective.[7] Five spots were taken randomly distributed over the surface, and the average surface roughness with standard deviation was examined as a function of total elapsed polishing time (Figure 1). It was found that it was possible to polish all glasses to between a 1 and 2 nm rms finish.

Figure 1- Roughness Over Time During Phosphate Polishing

Trial 1A, Polishing: rms- Roughness vs. Time

Trial 2, Polishing: rms- Roughness vs. Time

5.0 Characterization

5.1 Hardness

Hardness testing was done on a Tukon® Microhardness tester, with a 100 g load.[8] Knoop hardness numbers[9] were taken, but they had a large standard deviation. The indents were difficult to make in some glasses, and the results seemed unreliable compared to the Vickers measurements.[10] Ten hardness measurements were taken with a Vickers indenter over the polished surface to obtain average hardness numbers for all glasses.

5.2 Glass Transition Temperature

Glass transition temperature and softening point were measured using a Perkin Elmer Differential Scanning Calorimeter.[11] The instrument was calibrated immediately before use. Samples were prepared by removing shards of glass from parts and crushing them with a small hammer. Between 15 and 20 mg of crushed glass were weighed on an analytical balance and then sealed in shallow aluminum sample pans.[12] The pans were placed in the instrument along with an empty reference pan, where they were heated from $300^{\circ}C$ to $500^{\circ}C$ (note: LHG-8 had to be heated to $550^{\circ}C$ to obtain a complete thermal analysis curve) and scanned for heat flow. Each sample was heated twice. In the first heating, the onset of change in the thermal analysis curve provided the softening point. In the second heating, the onset of change in the thermal analysis curve provided the glass transition temperature.

5.3 Chemical Durability

Because water vapor in the air attacks the polished faces of phosphate glasses, a water durability test was chosen. Two samples of each melt were fine ground on all sides, using the orange bound abrasive pads, resulting in about 200 nm rms surface roughness. Sample size was measured using digital calipers and surface area was calculated. A typical sample was 26mm x 26mm x 12mm. Samples were cleaned using acetone and a drag-wipe method. They were then baked in a vacuum oven for 15 minutes at $50^{\circ}C$ to drive off any moisture. Samples were then weighed on an analytical balance, and immediately immersed in 900 ml of $50^{\circ}C$ DI water, agitated with a magnetic stir bar. After thirty minutes samples were removed, re-cleaned, re-baked and re-weighed. Most samples were then returned to their original beakers and suspended for an additional 30 minutes, and then re-cleaned, re-baked, and re-weighed. Gloves were used throughout this process to prevent oil/dirt from hands from being transferred to the samples.

Water durability was calculated as weight loss, per unit surface area, per unit time (or $mg/(cm^2*h)$). LHG-8 and 443 were tested under the same conditions for comparison. Trials 1A, 2 and 3 did not undergo these testing procedures because Trial 1C (which was tested) was essentially the same composition (see section 6.0). Trial 7 exhibited serious levels of devitrification and was not tested.

6.0 Composition Study

Table 1 gives the compositions of melts. Trial 1A produced a strongly discolored glass that was very green (rather than clear). Two more trials (Trial 1B and Trial 1C) were batched using the same composition and precursors, with extra care taken to remove any possible source of contamination (e.g. dirty crucibles, stirring rod, mortar and pestle), other than the precursors themselves. Trial 1B was never melted, but Trial 1C was melted, and was also very discolored. The barium oxide precursor was determined to be the source of the discoloration.

Trial 2 kept the same composition (see Table 1), however the source for the barium oxide was changed to barium carbonate. Because the carbonate would result in volatilization, the batch was preheated at 200°C for 4 hours prior to melting. This method was suggested in reference 1. The preheating did not appear to have had much effect, because significant bubbling was observed when the melt was placed in the oven. Trial 2 was clear.

Table 1- Trial Compositions in Mole Percent

Trial	P_2O_5	Na_2O	K_2O	Li_2O	BaO	CaO	ZnO	SnO	Al_2O_3	B_2O_3	Sb_2O_3	Dopant
Precursor	P_2O_5, Na_3PO_4, K_3PO_4, Li_3PO_4, $AlPO_4$	Na_3PO_4	K_3PO_4	Li_3PO_4	BaO for Trial 1, $BaCO_3$ for all others	$CaCO_3$	$ZnCO_3$	SnO	$AlPO_4$	H_3BO_3	Sb_2O_3	
1 (a-c)	33.94	7.81	7.81	3.91	13.45	13.45	13.45	none	0.43	1.39	4.38	none
2	33.94	7.81	7.81	3.91	13.45	13.45	13.45	none	0.43	1.39	4.38	none
3	33.93	7.81	7.81	3.91	13.44	13.44	13.44	none	0.43	1.39	4.38	Co_2O_3 0.02
4	37	8	5	7	8	14	14.5	none	0.5	1.5	4.5	none
5	37	8	5	7	8	14	14	0.5	0.5	1.5	4.5	none
6	35	8	5	7	10	14	14	0.5	0.5	1.5	4.5	none
7	31.58	8.42	5.26	7.37	10.53	14.74	14.74	0.53	0.53	1.58	4.74	none
8	34	8	8	4	11	14	14	1	1	0.5	4.5	none
9	33	8	7	4	13	13	13	1	2	1.5	4.5	none

The next composition, Trial 3, was essentially done to see if ionic colorants (useful as optical filter glasses) would be compatible with this type of composition. The composition was essentially kept the same, with 0.02% Co_2O_3 added (see table 2). This produced a glass with a good, deep-blue color.

It was suggested by one of the authors of reference 1 that tin oxide be added to the composition to improve durability. Trials 4 and 5 were done to investigate that idea. Trials 4 and 5 were similar compositions varying only by the addition of 0.5% SnO in Trial 5 (see table 2). Trial 5 proved to be more durable than Trial 4, so it was decided to include SnO in future compositions. Spectral scans were done using an HP Spectroscopy System[13] on parts with and without tin oxide, to verify that it was not having any effect on absorbance or transmission in the visible.

Trial 6 was done using a composition similar to Trial 5, except that the phosphorous pentoxide percentage had been lowered by two percent. Trial 7 had the phosphorus pentoxide content lowered an additional 1.5%. This trial did not form a glass, but instead crystallized.

Trials 8 and 9 were done with 34% and 33% phosphorus pentoxide, respectively (see Table 2). This was approximately the amount used in the initial trials. These compositions were melted to evaluate adjustments in the borate and alumina percentages. Both borate and alumina are known to strengthen the network in glasses, but it was not known what their effect would be on glass transition temperature.
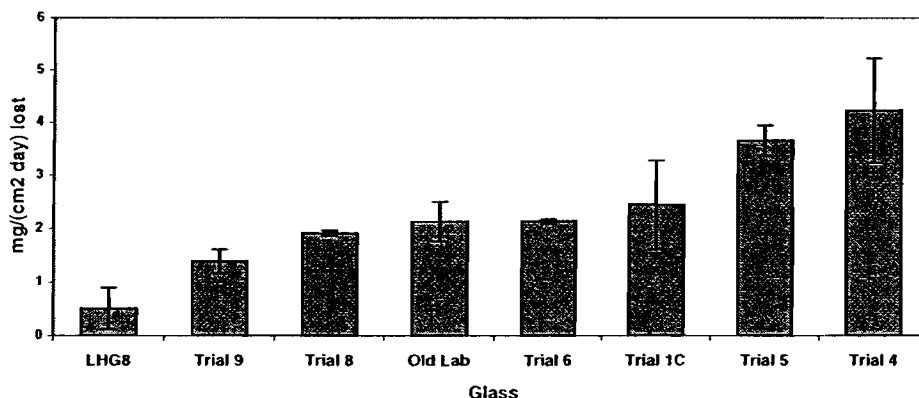
7.0 Summary of Results and Discussion

Results are summarized in Table 2 and Figure 2. The results are rank order in terms of decreasing durability.

Table 2 Summary of Characterization Results

Glass	Vickers Hardness Kgf/mm^2	Glass Transition $^{\circ}$C $\pm1\%$	Durability: Weight Loss mg/(cm^2 day)
LHG8	470 ± 33	498	0.5 ± 0.39
Trial 9	410 ±8	401	1.4 ± 0.21
Trial 8	420 ± 5	374	1.9 ±0.05
443	325 ± 5	432	2.1 ± 0.37
Trial 6	390 ± 6	380	2.1 ± 0.04
Trial 1C	375 ± 4	393	2.4 ± 0.83
Trial 5	395 ± 14	371	3.7 ± 0.29
Trial 4	395 ± 12	370	4.2 ± 1.00

Figure 2 Durability Defined By Weight Loss

Of all of the trials, Trial 9 was determined to be the best (see table 2). It had a chemical durability that while not near that of LHG-8, was much better than 443 (see figure 2). It
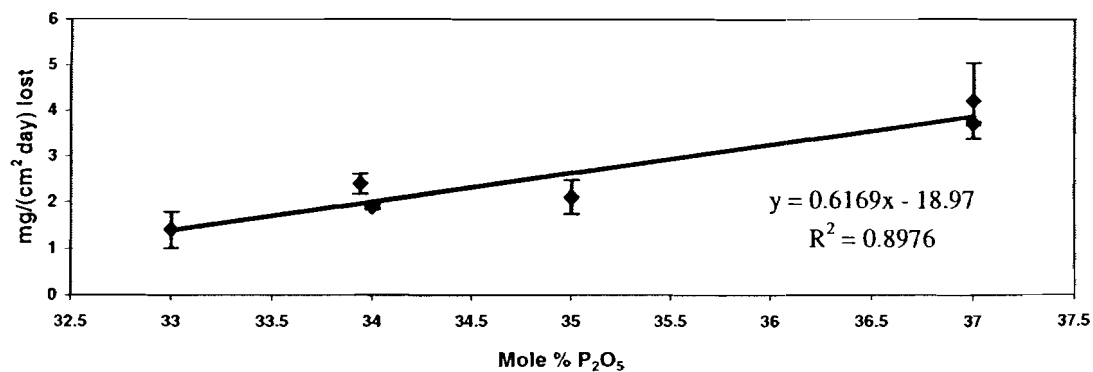
was reasonably hard, especially in comparison to 443. It also had a very desirable glass transition temperature, which was even lower than that of 443. This means that more composition adjustments could be made to increase the durability while keeping the glass transition temperature around $432^{\circ}C$ (the T_g of 443). The key to reaching this composition involved increasing the amount of alumina in the composition, adding tin oxide, and decreasing the amount of P_2O_5 as far as possible, without causing devitrification.

Alumina is known to improve durability, but it is also known to raise the glass transition temperature. Because of this it was present in very low percentages in earlier trials. However these trials had glass transition temperatures well below $432\,^{\circ}C$, and had poor durability. The composition was adjusted and it was found that it could include up to two percent alumina, with the glass transition temperature remaining low. This increase resulted in increased durability.

The effect of tin oxide was determined through Trial 4 and Trial 5. These compositions differed only in the addition of tin oxide to Trial 5. As can be seen in Figure 2 SnO increased durability. It also did not appear to affect glass transition temperature (see Table 2). As a result it was included in all new trials. Because of its ability to increase durability without increasing glass transition temperature, SnO would be a good constituent for study in future work with this type of glass.

As can be seen in Figure 3, phosphorous pentoxide content shows a strong correlation to weight loss in water. This makes sense because phosphorous pentoxide decomposes in water. However because it is the glass former, it is required in large quantities in the glass. Finding the lowest possible concentration was key. Trial 9, which had 33 percent phosphorous pentoxide, formed a glass and was the most durable. Trial 7, which had approximately 31.5 percent phosphorous pentoxide, had an unknown durability. This is because it crystallized and therefore was not tested. Optimum phosphorous pentoxide percentage for this glass appears to be approximately 33 percent.

Figure 3 Phosphorous Pentoxide vs. Durability

$y = 0.6169x - 18.97$
$R^2 = 0.8976$

Mole % P_2O_5

8.0 Conclusion

It is possible to make a relatively durable phosphate glass that also has a low transition temperature. To do so the glass former (phosphorous pentoxide) percentage must remain as low as possible. Alumina must be added in amounts greater than one mole percent and the correct balance between alumina and borate must be achieved. Lithium should be included, but its concentration should remain low. Tin is a possible additive that increases chemical durability, while creating no observable change in glass transition temperature.

Other observations and conclusions include the fact that care must be taken during the melting procedure to deal with volatilization; one possible means of doing so is ramping up from room temperature. Preheating below the melting point did not seem effective. For small parts the short annealing schedule used is acceptable. The use of 3M bound-abrasive Trizact pads allows this glass to be easily polished to the 1 to 2 nm rms roughness level. With our durability test on ground parts in water, error bars can be large for any given glass; this is not necessarily the best test procedure. Future work could include improvement of testing procedures. It could also include more modification of composition for improved qualities. Work could be done to dope this glass with colorants and rare earth ions, to study their effects in this glass.

9.0 Acknowledgments

10.0 References

1) "Improved Properties for Precision Molding Phosphate Glasses," Guorong Chen, Wen Liang and Jijian Cheng, Am. Ceram. Soc. Bul., p. 44 (March 2000)
2) LHG-8 is a Nd^{+3} doped phosphate laser glass manufactured by Hoya Corporation, 3400 Edison Way, Fremont, CA 94538
3) Colored Glass Melting Laboratory by Prof. Kathleen Richardson, developed for Optics 443: Optical Fabrication and Testing, a graduate course taught in The Institute of Optics at the University of Rochester
4) Wide Form Crucible, 250 ml, CoorsTek, Inc., VWR, 3000 Hadley Rd., So. Plainfield, NJ 07080

5) Graphite molds, approximately 5cm x 5cmx 4.5cm, producing glass cubes approximately 3cm x 3cm x 3.5cm

6) 3M™ Trizact™ Film. 3M Abrasive Systems Division; St. Paul, MN 55144-1000

7) Zygo New View™ 5000 White Light Optical Profiler, areal over 0.26 mm x 0.35 mm with a 20x Mirau objective, Zygo Corp., Middlefield CT.

8) Tukon® Microhardness Tester, Wilson Instruments, Binghamton, NY 13905

9) Knoop indenter certified by Wilson® Standards Laboratory, Wilson Instruments, Binghamton, NY 13905

10) Vickers Indenter certified by Wilson® Standards Laboratory, Wilson Instruments, Binghamton, NY 13905

11) Perkin-Elmer Differential Scanning Calorimeter 7, Perkin-Elmer Analytical Instruments, 761 Main Ave., Norwalk, CT 06859.

12) Perkin-Elmer sample pan kit no. 0219-0041, VWR, 3000 Hadley Rd., So. Plainfield, NJ 07080

13) Hewlett Packard 8453E Spectroscopy System, Hewlett-Packard, 3000 Hanover Street, Palo Alto, CA 94304-1185