

Section 3

ADVANCED TECHNOLOGY DEVELOPMENTS

3.A Ion-Exchange Strengthening of Nd-Doped Phosphate Laser Glass

Recent advances in high-repetition-rate and high-average-power (HAP) laser systems have put increasing demands on the thermal-loading capabilities of solid-state laser materials. In addition to the material's thermal properties, mechanical and optical limitations must also be identified if a reliable, high-performance system is to be maintained. After considerable effort in materials research at LLE and elsewhere, the physical limitations of various solid-state laser materials become better understood. This article describes specific efforts to increase the thermal-shock resistance of a commercially available, Nd-doped phosphate laser glass. Improvements in this physical property permit a glass to be pumped at levels that may previously have led to its fracture, resulting in a capability for higher-average output powers.

A recently completed HAP laser system at LLE, which serves as a high-repetition-rate source for the in-house damage-testing facility, consists of a phosphate-glass slab through which a beam propagates in a series of zig-zag, total internal reflections. Total internal reflection (TIR) makes efficient use of the entire gain medium. The slab is pumped and cooled on the two TIR sides, which reduces thermal beam distortion often present in alternative geometries. The slab can be operated in the single-pass mode (as an oscillator) or be multi-passed to additionally amplify the oscillator output. These features illustrate how the slab geometry lends itself well to HAP applications.

With renewed interest in HAP systems, emphasis needs to be placed on those properties of glass that make it a better HAP lasing

gain medium. It is essential that the gain of the glass be high if a compact system is to be capable of high average powers. The requirement for a low nonlinear index is not as relevant for these systems, since longer pulses (nanosecond vs picoseconds) are frequently used. However, the issues of chemical compatibility and ease of fabrication become increasingly important. Slabs in most HAP systems utilize continuous cooling provided by a liquid flowing at a relatively high velocity across the pump faces of the glass. The gain medium must be durable, as chemically induced degradation to the precision-polished TIR surfaces would adversely affect output performance.

Fabrication issues become exceedingly important with HAP systems. Slab geometries, in particular, require very tight tolerances. Large polished faces with sharp edges are required to be extremely parallel, flat, and of excellent surface (scratch/dig) quality. Polished Brewster-angle end faces need to be parallel to within arc seconds and of comparable, if not better, quality than the pump faces. For high-performance slabs these stringent fabrication requirements frequently cause high costs and long fabrication times.

The currently most limiting property of glass in HAP applications is its thermal-loading capability, specifically, its relatively low thermal-shock resistance. Byer¹ expresses the average laser power a HAP solid-state gain medium can withstand as the product of the material's thermal-shock resistance and the ratio of plate area to plate thickness. A material's thermal-shock resistance is directly linked to its strength, via the modulus of elasticity, the thermal expansion, and the thermal conductivity. These physical constants determine the stress limit, the fracture stress, at which a material will fail.

The thermal-shock resistance of a material, T_{SH} , is the temperature difference (ΔT) at which the fracture stress (commonly called the tensile yield stress) is reached and failure occurs. This relationship is illustrated in Eq. (1),²

$$T_{SH} = \frac{\sigma_f(1 - \mu)k}{\alpha E}, \quad (1)$$

where σ_f is the fracture stress, μ , k , E , and α are the material's Poisson ratio, thermal conductivity, Young's modulus, and linear coefficient of thermal expansion, respectively. Krupke³ examined the $(1 - \mu)k/\alpha E$ portion of the term as a material figure of merit (FOM). Data compiled for a number of crystalline and noncrystalline materials show that the FOM is much larger for crystals than for glasses. The FOM, coupled with each material's known tensile yield stress, indicates that crystals are several times more thermal shock resistant than glasses. Yet, crystalline materials of high optical quality and homogeneity are considerably more expensive than their glass counterparts and are in some cases simply unavailable in acceptable sizes. Because of these limitations, we have chosen to examine the potential of external treatments in improving the strength of

commercially available high-performance laser glass. Here we confine the discussion to Q-89, a phosphate-composition glass manufactured by Kigre, Inc.⁴

Any external strengthening treatment aims at introducing a compressive surface stress into the glass, in order to increase the stress required to fracture the glass in tension. Marion⁵ has shown that by reducing surface and subsurface damage in the form of microcracks (point sources where failure begins), via an acid etch, one can increase the fracture strength of a material. This benefit comes, however, at the expense of the optical surface quality and of the material's thickness, from which $\sim 200 \mu\text{m}$ are removed. Our alternative approach is to chemically treat the surface by way of an ion-exchange process (cracks included), in which the surface becomes stronger through the introduction of a layer of compressive stress to the glass surface. This ion-exchange strengthening can be performed without loss of optical surface quality.

Ion-exchange processing is routinely carried out by the glass industry in strengthening various products. The mechanism involves the exchange of a mobile alkali-ion A^+ that is present throughout the bulk material with a slightly larger ion B^+ of identical valence. The exchange is carried out in a molten-salt bath at an elevated temperature to accelerate the exchange of diffusing ions. The mobile A^+ ions readily diffuse out of the bulk, leaving vacancies behind. The larger B^+ ions migrate from the salt bath into the glass by occupying the small A^+ vacancies. The important feature of this "crowding" mechanism, as outlined by Kistler,⁶ is that it is performed at temperatures sufficiently below the strain point of the glass. An optimized treatment schedule prevents structural relaxation from occurring; as a result of the predominance of the larger ions, the surface is "expanded" into compression. A number of factors will control the net compressive stress that results from the process:⁷

- the radius ratio of the exchanging ions
- the degree to which the exchange occurs
- stress relaxation due to structural rearrangement of the surface
- any change in thermal expansion coefficient
- localized densification
- the depth of the compressive layer

Of these factors, the depth of the compressive layer is the most important. That layer can be thought of as a physical barrier that impedes the propagation of cracks. A thick layer will be more resistant to abrasion and thus failure, since any flaw would have to penetrate *past* this depth to initiate fracture.

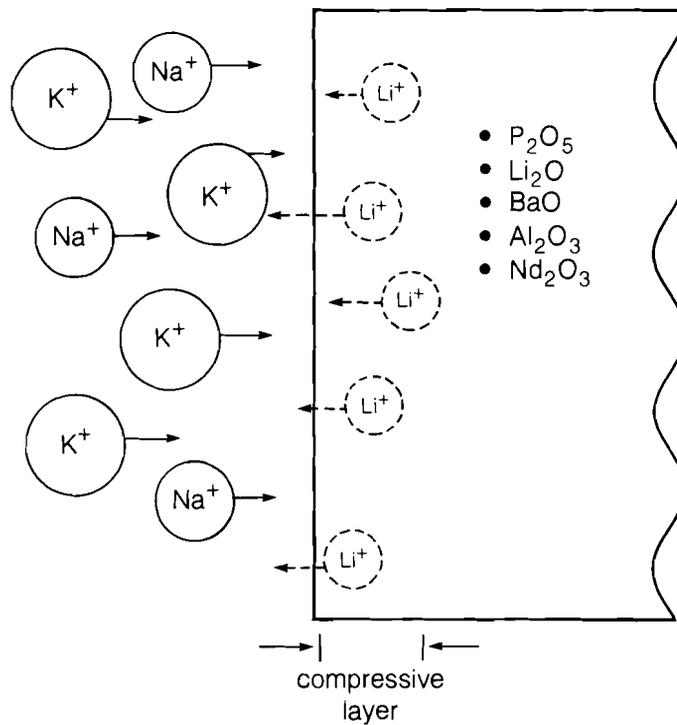
Considerable work has been done on the strengthening of silicate glass. To our knowledge, the process has not previously been extended to phosphate laser glass. While the basic mechanism remains the same, the composition of the base glass network determines the efficacy of the treatment. Silicates lend themselves well to ion exchange because their network consists of openly spaced

SiO₄ tetrahedra. This open network creates channels through which alkali ions can migrate easily.

The structure of phosphate glass is more complex. Whereas SiO₄ tetrahedra in silicate networks are able to bond to form similar tetrahedra, phosphate glasses are composed of PO₄ tetrahedra, which are limited in that they can only bond to three like structures during network formation.⁸ For this reason, Al₂O₃ is frequently added to assist as a network former in a phosphate-glass matrix. This, coupled with relatively large amounts of another network modifier, BaO, leads to a much more closed structure. This tighter matrix impedes the diffusion of alkali ions deep into the glass. Silicate glass systems strengthened via ion exchange obtain, therefore, thicker compressive layers than phosphates.

Fig. 25.24
 Ion-exchange mechanism in Kigre Q-89. Mobile Li⁺ ions diffuse out of the glass, leaving vacancies behind. Na⁺ and K⁺ ions preferentially diffuse from the bath into the Li⁺ vacancies, crowding into the smaller vacancies and creating a compressive layer on the glass surface.

The diffusion process that controls the exchange mechanism is very sensitive to changes in the exchange bath. Physical variations due to particulates, moisture, ion concentration, and other forms of bath contamination severely decrease the effectiveness of the process. In this work the primary A⁺ alkali ion is Li⁺, a major constituent in Q-89 in the form of Li₂O. The exchanging B⁺ ions are Na⁺ and K⁺, present in the bath as nitrate salts. Figure 25.24 depicts the ion-



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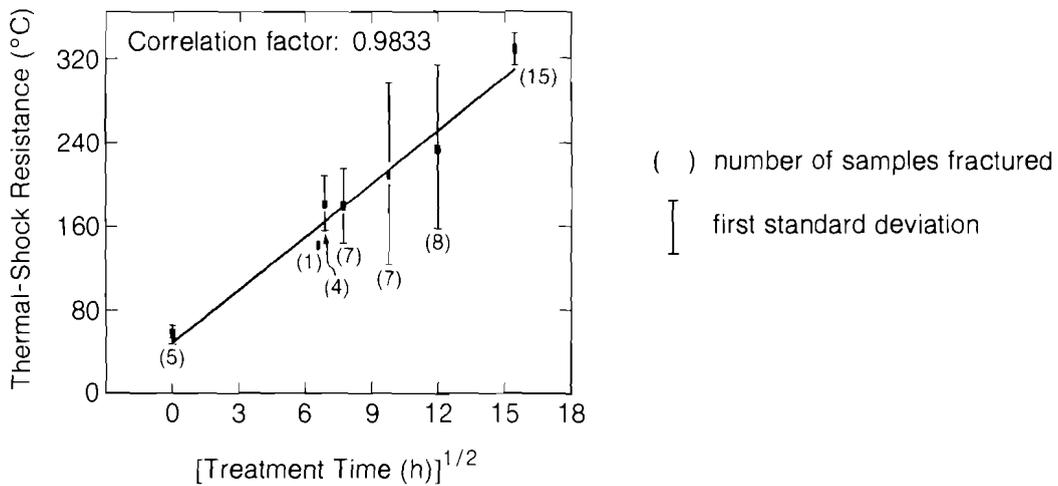
exchange mechanism in Q-89 and lists the other major constituents of this glass. The stoichiometry of the nitrate salts used in the bath is important; a large Na⁺/K⁺ ratio would be desired since Na⁺ is the predominant exchanging ion. However, Na⁺ is corrosive, and in applications such as these, where post-treatment surface quality is critical, a tradeoff must be made.

Several experiments have been conducted to examine methods for optimizing the strengthening process. The various test geometries and results are described as follows:

1. Thermal-shock tests

The improved strength through ion-exchange treatment was determined by a series of thermal-shock-resistance tests. Samples of Q-89 were fabricated into right-circular cylinders, 0.63 cm in diameter by 0.63 cm in length with fine-ground surfaces (#400 grit), acid etched in NH₄HF₂ for ~6 min prior to exchange treatment. The cylinders were then evaluated for their thermal-shock resistance through a soak/quench test. Treated cylinders were placed in an oven, raised to a prescribed temperature, and "soaked" at that temperature for ~30 min to guarantee sample-to-sample temperature uniformity. The samples were then removed and plunged into ice water (~5°-7°C). Upon removal from the ice bath, each sample was visually inspected for fracture. If no fracture occurred, the $\Delta T(T_{oven} - T_{water})$ was recorded and the process repeated at a soak temperature increased by +10°C. This continued until all samples had fractured. Results from these tests are shown in Fig. 25.25. Cylinders were treated in the exchange bath for 0, 2, 4, 6, and 10 days. The treatment time [in (hours)^{1/2}] is plotted in Fig. 25.25 versus measured

Fig. 25.25
Fivefold increase in thermal shock resistance in cylindrical, Q-89 samples. Excellent statistics ($\pm 5\%$) can be attributed to a clean, contamination-free bath.



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thermal-shock resistance, in °C. The treatment was carried out at an exchange-bath temperature of 320°C, with samples treated statically (no agitation) and removed and rinsed with de-ionized water every other day to remove any residual material buildup on the sample surfaces.

Introduction of a compressive layer through ion exchange resulted in a fivefold increase in thermal-shock resistance. Our thermal-shock test data show extremely small (approximately ±5%) standard deviations compared with the 50%–100% variation observed in data acquired through conventional mechanical-fracture techniques.

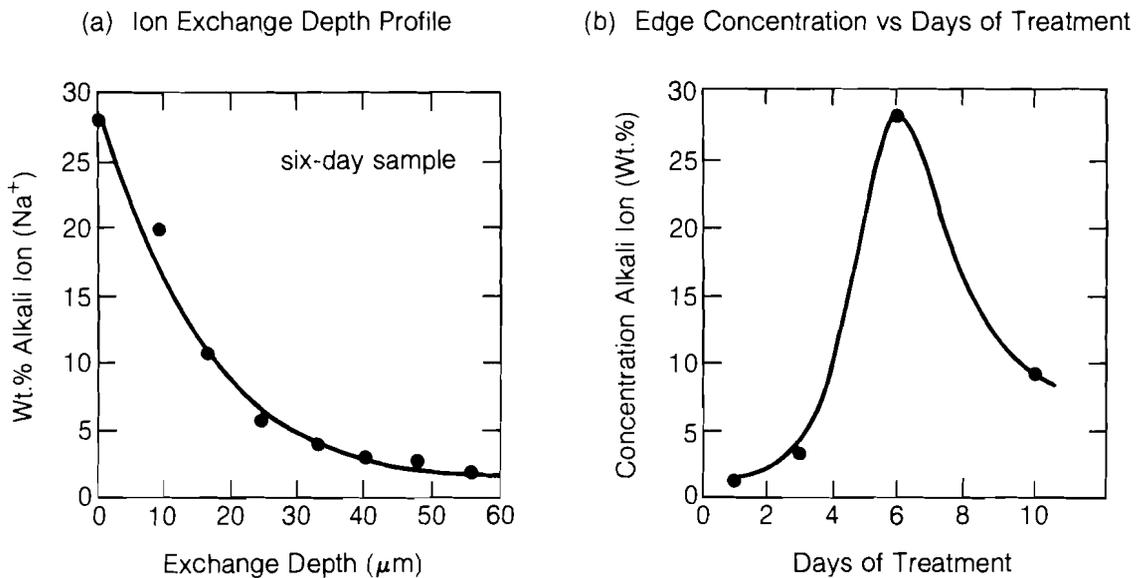
The widening spread in data for days 1–6 is a result of an increase in the level of bath contaminants. Depletion of diffusing ions and increased moisture content of the treatment bath are believed to have led to a larger standard deviation and poorer sample surface quality. The treatment of 15 samples for ten days in a new, dry bath restored the low standard deviation and improved sample surface quality. Although samples treated longer than ten days were not tested, it is important to note in Fig. 25.25 that we did not yet observe any leveling off in the strength improvement data. Thus, the ultimate levels of strength improvement are not known at this point and deserve further investigation.

Ion penetration depths of approximately 60 μm were measured via electron microprobe analysis.⁹ A depth profile for the light, highly mobile Na⁺ ion that preferentially diffuses into the glass is shown for a six-day treated sample in Fig. 25.26(a). Similar profiles for one-

Fig. 25.26

(a) Ion-exchange depth profile for six-day treated sample, as determined by electron microprobe analysis.

(b) Edge profile of alkali (Na⁺) ion concentration as a function of treatment time. Rollover after six days may be due to stress relaxation mechanism in glass network, which allows migration of Na⁺ ions away from surface and further into the bulk.



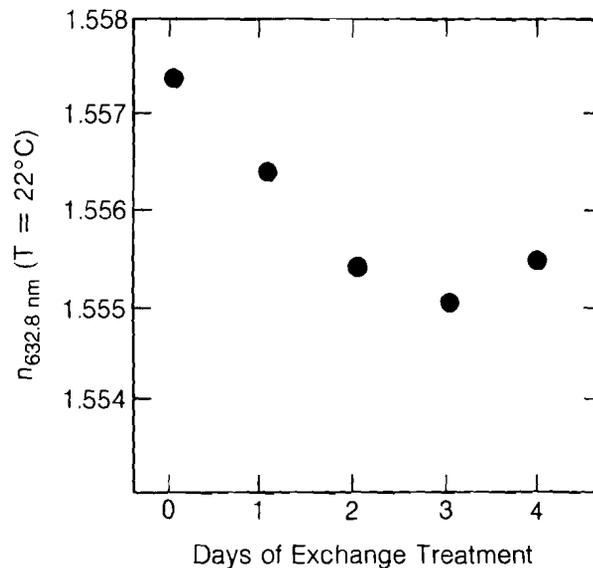
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through four-day samples showed an alkali-ion dropoff to the detection limit at depths of 35 to 40 μm . However, six- and ten-day samples remained at $\sim 3\%$ – 5% levels considerably further into the bulk. This observation is useful in explaining alkali-ion edge concentration data shown in Fig. 25.26(b). Here, we plot the edge concentration of alkali (Na^+) ions as a function of days of treatment. The rollover that occurs after six days may be due to stress-relaxation processes occurring in the glass network at the elevated bath temperature of 320°C . This stress relaxation could allow ions in high concentrations at the material's edge to migrate further into the bulk, thus decreasing the concentration at the edge.

Current work is focused on answering a number of questions relating to the details of the exchange mechanism. Reproducible profiles of light-ion concentrations are difficult to obtain and can be improved by fabricating samples with very clean edges. Supplemental analytical techniques will assist in confirming the details of the ion exchange, specifically in the analysis of the compressive layer.

2. Refractive-index variation in the surface layer

In examining the optical effects of the strengthening process, experiments were designed to investigate the new compressive surface layer. The surface refractive-index variations were measured as a function of days of treatment. A polished half cylinder was measured unstrengthened and then remeasured following additional one-day increments of treatment. These measurements were made on an Abbé refractometer, at $\lambda = 632.8 \text{ nm}$ and at a temperature of 22°C . The results of these tests are plotted in Fig. 25.27. The



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Fig. 25.27
Refractive-index variation in surface layer as a function of days of treatment. Measured index decreases as $\text{Li}_2\text{O}/\text{R}_2\text{O}$ ratio decreases.

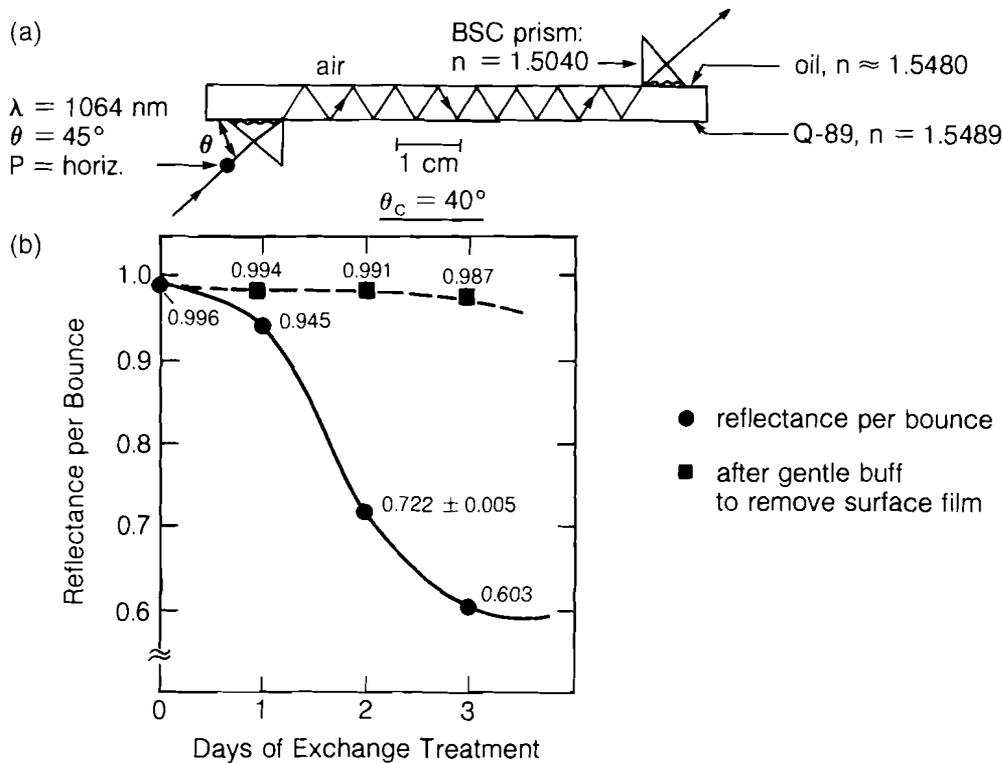
observed index decrease in the third decimal place is consistent with Kigre bulk-glass data for Q-89, which indicate a decrease in refractive index with decreasing $\text{Li}_2\text{O}/\text{R}_2\text{O}$ ratio. This decrease continues to occur in the strengthened layer with additional days of treatment. It is not expected that this small reduction in the surface index causes any deleterious effect on the TIR propagation of the beam through a strengthened slab.

3. TIR transmission tests

This experiment focused on treatment-induced degradation to optically polished surfaces. Thin slabs of Q-89, $15 \times 75 \times 3$ mm, were fabricated for TIR transmission measurements, at $\lambda = 1064$ nm and at a glass-air interface. The objective was to examine surface degradation and increased scatter as well as possible limitations to TIR as a function of exchange-treatment time. Measurements on treated slabs were compared with the transmission through an untreated control sample. A YAG ($\lambda = 1064$ nm) laser was injected at $\sim 45^\circ$ ($>$ critical angle, $\theta_c = 40^\circ$) into the slab through a BK-7 prism, which was index-matched to the Q-89 surface, as shown in Fig. 25.28(a). After a series of TIR bounces the beam exited the sample and the total transmission drop was monitored. From this observation the reflectance per bounce was calculated. The result is shown as a solid line in Fig. 25.28(b).

Fig. 25.28

(a) Total internal reflection (TIR) experiment on thin slabs of Q-89 at $\theta = 45^\circ$ and $\lambda = 1064$ nm; measurements were made in air. (b) Reflectance per bounce decreases as a function of days of treatment. Gentle buff of treated surface restores TIR reflectance to the $>99\%$ level.



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Surface films may become apparent after as little as three days of treatment. Visible inspection of the samples after treatment showed a very irregular, mottled film, which gradually worsened with treatment time. This film caused the steady drop in reflectance that was observed as treatment time was lengthened. A gentle buff removing the surface film was found adequate to restore TIR reflectance to the 99% level. Minimal ($<0.5 \mu\text{m}$ for three-day sample) material removal was required to achieve this improvement. This encouraging test was based on a worst-case experiment, due to the use of an old, contaminated salt-bath treatment of that sample. We suspect that the observed surface film is the result of moisture contamination in the bath,¹⁰ which can be eliminated with proper preventive measures.

The details of the process as outlined here support the claim that phosphate laser glass can be strengthened effectively. The demonstration of a fivefold increase in thermal-shock resistance of Q-89 illustrates the potential of this technique. A first step in assessing the impact of the ion-exchange process on the optical surface quality of fabricated parts is completed.

Several issues are unresolved. Work is continuing to address the issues of bath contamination, optical surface degradation due to moisture, the effect of exchange treatment on the interferometric quality of fabricated parts (optical surface deformation due to compressive stress), and the compositional gradients of the compressive-stress layer. Scalability of current results from test-specimen scale to full-sized slab samples is of major importance. Results from these investigations will further enhance the capabilities of high-average-power laser systems with phosphate-glass gain elements.

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