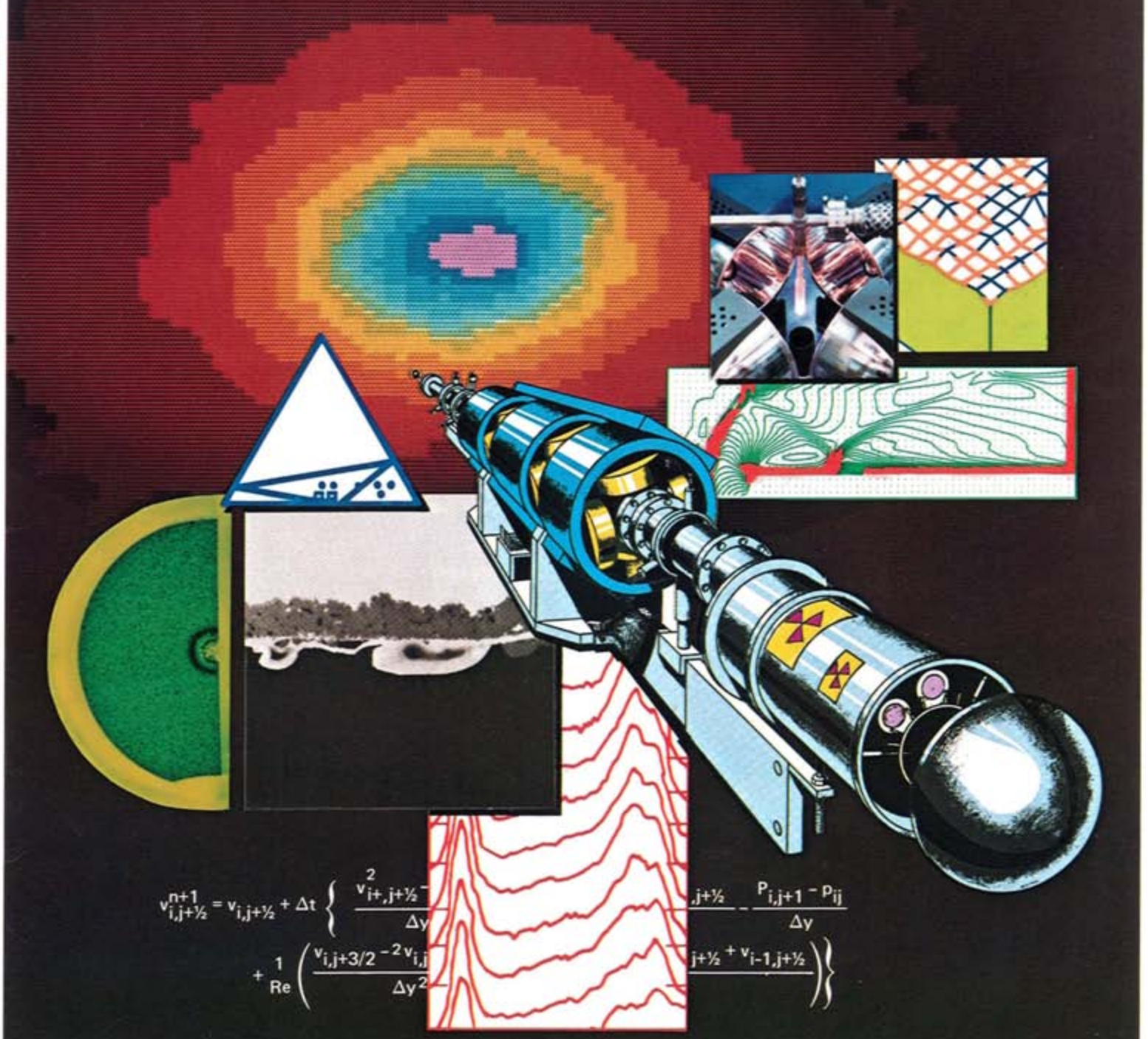
Energy and Technology Review

Lawrence Livermore Laboratory
November 1979

BASIC ENERGY SCIENCES I



$$v^{n+1}_{i,j+½} = v_{i,j+½} + \Delta t \left\{ \frac{v^2_{i+,j+½} - \quad ,j+½ - \frac{P_{i,j+1} - p_{ij}}{\Delta y}}{\Delta y} + \frac{1}{Re}\left(\frac{v_{i,j+3/2} - 2v_{i,j} \quad j+½ + v_{i-1,j+½}}{\Delta y^2} \right) \right\}$$

could be a useful screening technique for selecting candidate alloys in coal-conversion systems. The smaller the passive current for an alloy, the better its chances of surviving in coal-conversion environments.

We are also carrying out experiments at constant applied potential for various lengths of time to determine the kinetics of scale growth under anodic and cathodic conditions. We hope to be able to correlate these rate constants with those determined by thermogravimetric analysis in comparable conditions.

Future plans. Our next step is to study binary alloys of nickel with aluminum, chromium, and iron. Also, we will be studying how thermal cycling and stress affect hot-corrosion attack on pure metals and simple alloys.

For further information contact John J. Truhan (422-6925).

Key words: coal conversion; corrosion; corrosion prevention; hot corrosion; materials—corrosion; metals—oxidation; oxidation.

Nonlinear effects in optical materials

In high-power lasers, with intense radiant fluxes and with optical elements operating close to their damage thresholds, the properties of the transparent optical materials become critical. We are studying two nonlinear interactions that affect the efficiency of laser glasses. One is nonlinear contributions to the refractive index, which cause self-focusing, runaway intensification of hot spots in the beam, and loss of beam coherence. The second is two-photon absorption, which causes optical losses and may be an important damage mechanism in the near-ultraviolet and ultraviolet range. We found that fluoride glasses, especially the fluoroberyllates, are excellent candidates for optical components. They have a small coefficient of nonlinear refractive index, and they show better gain than silicate glasses. We will examine the nonlinearity of the refractive index at shorter wavelengths and longer time intervals, and we will study two-photon absorption in not only the fluoroberyllates but also the alkaline and alkaline-earth halides, silicate and phosphate glasses, and nonlinear electrooptic materials.

The development of high-power lasers, particularly neodymium-glass lasers for fusion research, has placed stringent requirements on the properties of transparent optical materials. The electric fields associated with the light beams propagated in our Shiva laser are so intense that nonlinearity in the polarizability of the transmitting material becomes important. Two nonlinear interactions of interest for future high-power lasers are nonlinear contributions to the refractive index, which cause self-focusing, and two-photon absorption, which causes optical losses. We are studying both of these nonlinear effects in a search for ways to improve laser materials.

Nonlinear refractive index. The nonlinear refractive index is one of the most important optical properties affecting the performance of short-pulse, high-power fusion lasers. The refractive index of a material is given by

$$n = n_0 + \Delta n ,$$

where n_0 is the linear refractive index and Δn is the intensity-

dependent change in the refractive index. The index change Δn is given by $n_2\langle E^2\rangle$, where n_2 is the nonlinear refractive index and E is the amplitude of the optical electric field.

There are two main causes for the nonlinearity of the refractive index: the polarizability of the cloud of electrons around individual atoms (nuclei considered motionless), and the polarizability arising from various types of nuclear motion—vibrations, reorientation, etc.—depending on the degrees of freedom of the material constituents.

For beam intensities of about 10 GW/cm^2, the change in refractive index is only a few parts per million. What makes this small change significant is the total path length (which may exceed 1 m) through optical materials in the long amplifier chains of fusion lasers. Self-focusing causes beam distortion at high power and, if uncontrolled, can degrade the ability to focus on the target (and hence reduce the energy delivered) and even permanently damage the optical components by concentrating the beam energy into hot spots that exceed the damage threshold.

Our early experiments revealed that material with a small linear refractive index, n_0, and a small wavelength dispersion also had a small nonlinear index coefficient, n_2. We have obtained further data on the correlation between linear and nonlinear refractive indices for a wide variety of crystals and glasses by time-resolved interferometry.[1] Combining these results, obtained at 1.06 μm, with certain empirical relationships,[2] we can estimate the nonlinear index from measurements of the linear index and the dispersion.

Optical glasses are conveniently grouped by using as coordinates the refractive index n and the Abbe number ν, where ν is the reciprocal of the dispersion. Regions of n_d and ν_d of known optical glasses are shown in Fig. 1. (The subscript signifies that the properties were measured at the wavelength of the helium d line, 587.6 nm.) Superimposed on Fig. 1 are dashed lines of constant n_2 predicted from n_d and ν_d values.[2] To propagate laser beams with small distortions, we need low-n_2 glasses (the fluoride-containing glasses in the lower left).

The most common commercial optical glasses are oxide glasses, principally silicates and phosphates (i.e., SiO_2- and P_2O_5-based). Current optical glasses with the lowest n_2 values are fluorine-containing oxide glasses, the fluorosilicates and fluorophosphates. The glass with the smallest refractive index is BeF_2 without any modifiers.[3] BeF_2 forms a glass analogous to SiO_2, but it is more ionic and has weaker bonds (and hence a lower melting point).

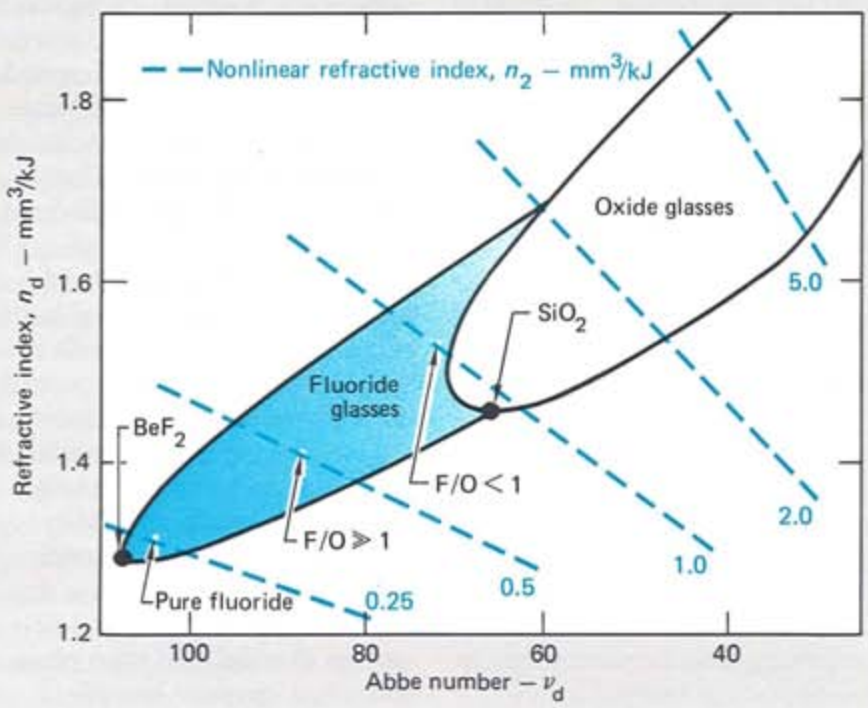


Fig. 1 *Classification of optical glasses by the refractive index, n_d, versus the Abbe number (reciprocal of dispersion), ν_d. Dashed lines indicate contours of constant nonlinear refractive index, n_2, as shown by our measurements. We are developing optical materials with the lowest possible n_d, ν_d, and n_2, such as beryllium fluoride glass.*

Figure 1 shows pure BeF_2 and SiO_2 glasses, which represent the lowest n_2 values of the fluoride and silicate glass types, respectively. The addition of network modifiers such as alkalis, alkaline earths, aluminum, and other cations changes the optical properties and yields the n_d–ν_d regions shown.

Because of their predicted small values of n_2, fluoride glasses are the most promising candidates for both passive components (such as lenses, windows, and substrates) and active components (such as the laser-amplifier and Faraday-rotation media) in short-pulse, high-power lasers. Since fluoride glasses generally have large band gaps, they transmit light over a large spectral range. Hence they are potentially useful as transmitting optical components for high-power lasers operating at short wavelengths into the vacuum ultraviolet (VUV) region.

Our studies of the nonlinearity of the refractive index are being extended to shorter wavelengths and longer time intervals. Most of our data have been gathered at a wavelength of 1.06 μm, but we will soon be experimenting with light at one-half, one-third, and one-quarter of this wavelength (532, 355, and 266 nm). This effort will enable us to measure the wavelength dispersion of n_2, both in regions of transparency and as the input wavelength approaches material absorption bands where resonant enhancement of n_2 is possible.

In the time domain, we are using a new variable-pulse-duration laser that will enable us to observe the growth of the electrostrictive and thermal components of n_2 and to obtain the first accurate measurement of these behaviors on a nanosecond time scale. These additional contributions to n_2 may have important implications for high-power, long-pulse lasers.

Nonlinear absorption. A second thrust of our program is the study of nonlinear absorption phenomena in transparent solids. The lowest order of these phenomena, two-photon absorption (TPA), is regularly observed in studies of various visible and ultraviolet (UV) high-power lasers (such as rare gas, rare-gas halide, and excimer lasers). The progression of familiar laser-induced material damage mechanisms such as avalanche ionization into the multiphoton limit is of fundamental interest to physicists. In the near-UV and UV, we expect TPA to be an important damage mechanism.

We have constructed a dual monochromator system operating in the UV and VUV regions that will be used to record TPA spectra for the first time in materials with wide band gaps and absorption edges in the VUV. We will also be performing linear spectroscopy to determine accurately the fundamental absorption-edge and impurity-absorption characteristics of these materials.

In addition, we will be measuring both the absolute TPA coefficients at harmonics of the optical wavelengths of our neodymium-glass laser and the TPA spectra for important optical materials such as the alkali and alkaline-earth halides; silicate, phosphate, and fluoride glasses; and nonlinear electrooptic materials such as KDP, ADP, and CDA (potassium dihydrogen phosphate, ammonia dihydrogen phosphate, and cesium dihydrogen arsenate, respectively). By employing combinations of linearly and circularly polarized pulses, we expect to obtain, in selected cases, four independent spectra of materials in cubic group O_h, each of which corresponds to an irreducible representation of the TPA tensor operator. These results will be of theoretical value for band-structure models and will provide much-needed experimental data for optimal UV window materials.

Materials synthesis. The preparation of beryllium fluoride glasses involves a number of problems,[4] not the least of which are the toxicity and special handling requirements of beryllium and the need to exclude moisture during handling and processing of the reactive powdered ingredients. We weigh and mix high-purity (99.99%) fluorides and diammonium beryllium tetrafluoride [$(NH_4)_2BeF_4$] powders in a dry, inert atmosphere (nitrogen or carbon dioxide) and then place them in a graphite crucible. Induction heating drives off ammonium fluoride and fuses the powders into a glass. After the first decomposition we are able to use platinum crucibles for further heating cycles.

Polishing a piece of beryllium fluoride glass is a crucial operation

because these glasses require a low-moisture environment and good temperature control. We have investigated a wide variety of standard polishing media and established a set of parameters for obtaining satisfactory optical finishes. We have also measured the solubility of beryllium fluoride glasses in water as compared with those of other optical glasses and crystals.[5]

We are also conducting phase-equilibrium studies of mixed beryllium and aluminum fluoride crystal systems. If we identify any suitable phases, we will explore the crystal growth characteristics of the system. We also have equipment for measuring thermal expansion, thermal conductivity, hardness, and modulus of rupture of such new materials. Table 1 gives the range of physical and fluorescence properties we have obtained from the beryllium fluoride glasses investigated thus far, principally those in the low-index region of Fig. 1.

Lasing properties of fluoroberyllate glasses. Since the advent of lasers, thousands of glasses have been formulated to investigate the effects of changes in glass network and network-modifier ions on the spectroscopic and lasing parameters of neodymium.[6] The host glass has an important influence on the ability of the lasing ion to absorb light from the optical pumping source, to store this energy, and to release it to amplify the laser beam. Energy storage by the lasing ion is governed by its absorption properties, excited-state lifetimes, and quantum efficiency. For rare-earth laser glasses, the energy-storage capability varies only slightly with the host glass. The rate of energy extraction, on the other hand, is governed by a product of the optical intensity of the extracting beam and the stimulated-emission cross section σ of the lasing ions. Both of these factors are strongly influenced by the characteristics of the host glass. Hence by appropriate choice of the host glass we can produce lasers with widely varying performance.

The optimum cross section depends on the intended operation of the laser. For a short-pulse, unsaturated laser, we need a high cross section for large gain with a minimum thickness of glass, although the cross section must be set low enough to avoid parasitic losses (in large amplifiers) and saturation. On the other hand, long-pulse saturated lasers require low, homogeneous cross sections that allow storage and extraction of large amounts of energy without parasitic losses or hole burning, although the cross section must not be so low that excessive flux, capable of causing nonlinear optical distortion, would be required to extract the energy. Thus for any fixed pulse width there is an optimum cross section.

Figure 2 shows the results of our gain measurements[7] for three neodymium-glass types. Although

Table 1 *Ranges of properties measured for various beryllium fluoride glass compositions.*

Physical properties	
Density, g/cm^3	1.99–3.3
Refractive index n_d	1.28–1.4
Nonlinear index n_2, mm^3/kJ	0.23–0.4
Thermal expansion, 10^{-6}/K	7–20
Thermal conductivity, W/μm·K	80–90
Knoop hardness, kg/mm^2	180–315
Young's modulus, GPa	36–50
Shear modulus, GPa	14–20
Poisson's ratio	0.15–0.28
Fluorescence properties for Nd^{3+} $^4F_{3/2} \longrightarrow {}^4I_{11/2}$	
Peak wavelength, μm	1.046–1.050
Emission cross section, pm^2	1.7–4.0
Linewidth (FWHM), nm	15–24
Lifetime, μs	530–1000
Branching ratio	0.49–0.51

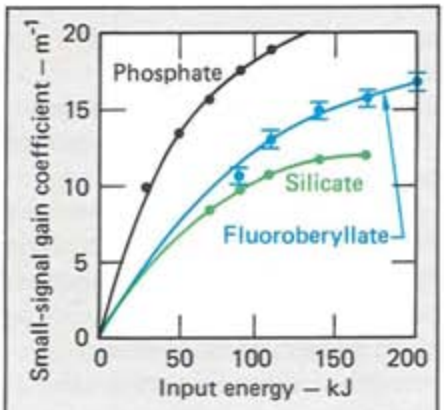


Fig. 2 *Measured and calculated small-signal gain coefficients for three neodymium glasses. Beryllium fluoride glasses provide a higher gain than either silicate or phosphate glasses.*

Table 2 *Representative relative figures of merit for different glass types, using neodymium-laser cross sections. Changing composition can produce variations within a given glass type.*

Component	Figure of merit	Silicate glass	Phosphate glass	Fluoro-phosphate glass	Fluoro-beryllate glass
Laser rod (pump limited)	$\frac{\sigma n}{n_2}$	1.0	2.3	2.3	4.2
Laser disk (pump limited)	$\frac{\sigma n^2}{n_2}$	1.0	2.2	2.1	3.6
Laser disk (parasitic limited)	$\frac{n^2}{n_2}$	1.0	1.4	2.3	3.1
Window	$\frac{n}{n_2}$	1.0	1.5	2.0	3.6
Lens	$\frac{n(n-1)}{n_2}$	1.0	1.3	2.0	2.2

the fluoroberyllates have lower gain than some other glasses we have measured, they are better in this respect than the silicates. Other compositions containing large amounts of beryllium and aluminum fluorides also provide lasing media with low cross sections and good energy storage.

Table 2 gives figures of merit for the various glass types, combining the effects of nonlinear refractive index n_2 and cross section σ. For short-pulse operation where n_2 is important, fluoride glasses offer superior performance.

Summary. We are investigating the nonlinear effects that limit the energy flux a laser can safely deliver. These include the nonlinear portion of the refractive index, which degrades beam coherence and tends to amplify small perturbations in beam uniformity into potentially damaging hot spots, and two-photon absorption processes that convert laser energy into intense local heat. We are developing a number of new optical glasses, especially the beryllium fluorides, with extremely low nonlinear indices of refraction. Our results to date indicate that fluoroberyllate compositions would form a suitable glass for high-power laser applications.

For further information contact Marvin J. Weber (422-5486).

Key words: absorption, nonlinear; beryllium fluoride glass; glass lasers; lasers—materials; neodymium glass; refractive index, nonlinear.

Notes and references

1. M. J. Weber, D. Milam, and W. L. Smith, "Nonlinear Refractive Index of Glasses and Crystals," *Optical Eng.* **17**, 463 (1978).
2. N. L. Boling, A. J. Glass, and A. Owyoung, "Empirical Relationships for Predicting Nonlinear Refractive-Index Changes in Optical Solids," *IEEE J. Quantum Electron.* **QE-14**, 601 (1978).
3. M. J. Weber *et al.*, "Measurements of the Electronic and Nuclear Contributions to the Nonlinear Refractive Index of Beryllium Fluoride Glasses," *Appl. Phys. Lett.* **32**, 403 (1978).
4. C. F. Cline and M. J. Weber, *Beryllium Fluoride Optical Glasses: Preparation and Properties*, Lawrence Livermore Laboratory, Rept. UCRL 81168 (1978). Presented at the First International Otto Schott Symposium, Jena, D.D.R., July 1978.
5. C. F. Cline, D. D. Kingman, and M. J. Weber, "Durability of Beryllium Fluoride Glasses in Water: Comparison with Other Glasses and Crystals," *J. Non-Cryst. Solids* **33**, 417 (1979).
6. Previous work on glasses for high-power fusion lasers was described in *Energy and Technology Review* for September 1977 (UCRL-52000-77-9), p. 16.
7. G. J. Linford, R. A. Saroyan, J. B. Trenholme, and M. J. Weber, "Measurements and Modeling of Gain Coefficients for Neodymium Laser Glasses," *IEEE J. Quantum Electron.* **QE-15**, 510 (1979).