✓
MASTER

UCRL-84399

PREPRINT

CONF-800552--1

PROPERTIES OF LOW-INDEX
LASER MATERIALS

by
Marvin J. Weber

This paper was prepared for submittal to
Topical Conference on Basic
Optical Properties of Materials
May 5-7, 1980
Gaithersburg, Maryland

May 9, 1980

The logo for Lawrence Livermore Laboratory, featuring a stylized 'L' and the text 'Lawrence Livermore Laboratory' in a bold, sans-serif font, oriented diagonally within a rectangular frame.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

PROPERTIES OF LOW-INDEX LASER MATERIALS *

M. J. Weber

Lawrence Livermore Laboratory
University of California
Livermore, California 94550

MASTER

The use of large, high-power lasers for inertial confinement fusion experiments has prompted the search for improved optical materials.¹ These include glasses and crystals for both passive components (lenses, windows, substrates) and active components (amplifiers, Faraday rotators). Neodymium-doped glass lasers, which operate at $\approx 1\mu\text{m}$, have been the most widely used fusion lasers. Of major concern for these lasers are (1) the nonlinear optical properties, including intensity-dependent changes in the refractive index, multiphoton absorption, and damage processes, and (2) the spectroscopic properties of the active laser ion which affect energy storage and extraction and the overall lasing efficiency. To reduce self-focusing and beam break-up, materials for the amplifying medium and transmitting optics must have a small nonlinear refractive index n_2 . This is characteristic of low-refractive-index materials. In the past few years, the optical properties and preparation of many low-index materials have been investigated. From this search, fluoride crystals and glasses have emerged as superior optical materials for short-pulse high-power lasers. Of these, fluorophosphate^{2,3} and fluoroberyllate^{4,5} glasses have received particular attention.

The large variety of inorganic glass forming systems⁶ provides many opportunities to tailor materials for specific applications. Optical properties are generally most affected by the glass network former, however within a given glass type, further variations are possible by the selection of the network modifier cations. The optical properties of Nd³⁺ in hundreds of oxide, fluoride, and oxyfluoride glasses have been investigated to determine the range of variations possible by altering the host glass composition. Examples of the ranges of optical and spectroscopic properties observed for some common oxide and fluoride glasses are summarized in Table I. These represent values observed to date at the Lawrence Livermore Laboratory, but are not necessarily the extreme values possible. Depending upon the mode of operation and the environment of the laser, other physical and chemical properties may also be important. All of these properties are dependent, in varying degrees, on the chemical composition of the host.

Measurements of n_2 for a large class of oxide and fluoride crystals and glasses have been made using 100-ps, 1.06- μm laser pulses and time-resolved interferometry.⁷ Values of n_2 for various glasses are summarized in Table I. These results established that low-index,

*Work performed under the auspices of the U. S. Department of Energy Office of Basic Energy Sciences and the Lawrence Livermore Laboratory under contract Number W-7405-ENG-48.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Reg

TABLE I. Observed variations of Nd laser glass properties.
Spectroscopic properties are for the $^4F_{3/2} \rightarrow ^4I_{11/12}$ transition.

Glass	NL Index $n_2(10^{-13} \text{ esu})$	Cross Section $\sigma(\text{pm}^2)$	Linewidth $\Delta\lambda_{\text{eff}}(\text{nm})$	Lifetime $\tau_R(\mu\text{s})$
Silicate	≥ 1.2	1.0-3.6	34-43	170-950
Phosphate	≥ 1.0	1.8-4.7	23-34	320-560
Tellurite	> 10	3.0-5.1	26-31	140-240
Fluorophosphate	≥ 0.5	2.2-4.3	27-34	350-600
Fluoroberyllate	≥ 0.3	1.7-4.0	19-28	550-1000

low-dispersion materials have small n_2 values. These are materials having low atomic number anions and cations and small optical polarizabilities. Boling, Glass, and Owyong⁸ have discussed various empirical relationships that can be used to predict the nonlinear index based upon simple measurements of the linear index and dispersion. These relationships provide valuable guidance for screening materials.

For short pulse durations and large beam diameters, the principal refractive index nonlinearity arises from the optical Kerr effect. For longer pulses ($> 1\text{ns}$), electrostrictive effects may become important. These contributions have been found to be smaller for low-index materials.⁹

Most n_2 measurements in solids have been made at wavelengths far removed from the fundamental absorption edge. At shorter wavelengths, n_2 will increase due to resonant and nonresonant contributions to the wavelength dispersion of n_2 .¹⁰ This consideration is germane for fusion lasers such as KrF (248 nm) or the use of higher harmonics of Nd lasers (532, 355, 266 nm). At present, however, there is no data on the magnitude and functional dependence of the wavelength dependence of n_2 .

Low-index materials are generally wide band gap materials.¹¹ Therefore materials selected to reduce self-focusing will probably also have small linear and nonlinear absorption. At ultraviolet wavelengths, most materials are subject to two-photon absorption (TPA). TPA coefficients at short wavelengths are known for only a few optical materials.¹² Measurements of TPA spectra of a variety of materials are needed to select laser materials with minimum losses at short wavelengths.

TABLE II. Comparison of Nd:fluoroberyllate laser glasses.

Composition (mol. %)	98 BeF ₂ + 2 NdF ₃	58 BeF ₂ + 32 KF + 6 CdF ₂ + 2NdF ₃	47 BeF ₂ + 27 KF + 14 CaF ₂ + 10 AlF ₃ + 2NdF ₃
⁴ F _{3/2} → ⁴ I _{11/2} Spectroscopic Properties:			
λ _p (nm)	1046	1048	1047
σ(pm ²)	2.0	3.8	3.2
Δλ _{eff} (nm)	27.7	20.1	23.2
τ _R (μs)	920	600	610
Relative Small-Signal Gain Coefficient: ¹⁵			
g (m ⁻¹)	7.8	17 (estimate)	14.8

Laser-induced damage thresholds of materials have also been found to vary with refractive index. Bettis, Guenther, and House¹³ have measured damage thresholds for surfaces and thin films of many materials at 1.06 μm. They find a systematic increase in damage fluence with decreasing refractive index. Low-index fluoride materials have the highest damage thresholds. This behavior continued to hold at shorter wavelengths.¹⁴

Whereas low-index materials are clearly superior based on their non-linear optical properties and laser-induced damage thresholds, for the amplifying medium, the effects of compositional changes on the spectroscopic properties must also be considered. From Table I we see that the Nd³⁺ stimulated emission cross section σ can be varied by more than a factor of 5. There are corresponding large changes in the radiative lifetime τ_R. For xenon flashlamp pumping, the population inversion obtainable in various glasses in a standard test setup are comparable, but the small-signal gain coefficient varies because of the different σ values.¹⁵ Therefore glasses having large cross sections, such as phosphates, have large gain coefficients. By varying the composition,

fluoroberyllate glasses having either small or large cross sections and gain coefficients are possible. Several examples are given in Table II and in Ref. 4. The spectroscopic variations achieved for Nd^{3+} should also be obtained for other rare-earth laser ions.

The absorption and emission spectra and gain profile of rare earths in glass are inhomogeneously broadened because of site-to-site differences in the local environment of the laser ion. This structural disorder is not evident in amplifiers operating under small-signal conditions, but under large-signal or saturated gain conditions, spectral hole burning may occur.¹⁶ In addition, the energy extracted from an inhomogeneous system is always less than that obtainable from a homogeneous system having the same initial small-signal gain.

To minimize these effects, one seeks materials in which the ratio of the homogeneous to inhomogeneous linewidths is as large as possible. The effective fluorescence linewidth in Table I is a measure of a combination of the extent of the crystalline Stark splitting of the initial and final J manifolds and the inhomogeneous broadening. Of the glasses studied to date, fluoroberyllate glasses have the narrowest effective linewidths. Our knowledge of the effects of glass composition on the homogeneous linewidth, on the other hand, is still very limited. Laser-induced fluorescence line narrowing techniques are used to measure the homogeneity of the spectroscopic properties in glass.¹⁷ The homogeneous linewidths of oxide and fluoride glasses measured thus far do not differ greatly.¹⁸ Therefore fluoroberyllate glasses should have good saturation properties. Additional studies of the homogeneous linewidths for a wider range of glasses are underway.¹⁹

Of the various low-index materials, fluoroberyllate glasses have the smallest refractive index nonlinearly and a large range of transparency. Inclusion-free materials have high damage thresholds.²⁰ Fluoroberyllate glasses have now been prepared by the Corning Glass Works²¹ in sizes up to 20-cm diameter by 5-cm thick. The toxicity of beryllium necessitates special handling requirements for the melting and finishing of these glasses. The hygroscopicity of BeF_2 is well known, but by the addition of suitable modifier cations, the chemical durability can be greatly improved. Although the water solubility is still greater than for most commercial optical glasses, it is less than for many alkali halide optical crystals.²²

Acknowledgments

Many colleagues at LLL have contributed to the results summarized in this paper. It is a pleasure to thank S. Brawer, C. Cline, D. Kingman, G. Linford, J. Lynch, D. Milam, R. Saroyan, W. L. Smith, A. Glass, S. Stokowski, and J. Trenholme.

References

- ¹M. J. Weber, "Optical Materials for Neodymium Fusion Lasers," in *Critical Materials Problems in Energy Production*, ed. C. Stein (Academic Press, New York, 1976), p. 261.
- ²O. Deutschbein, M. Faulstich, W. Jahn, G. Krolla, and N. Neuroth, "Glass with a Large Laser Effect: Nd-Phosphate and Nd-Fluorophosphate," *Appl. Optics* 17, 2228 (1978).
- ³J. T. Wenzel, D. H. Blackburn, W. K. Haller, S. E. Stokowski, and M. J. Weber, "Development of Fluorophosphate Optical Glasses," SPIE Vol. 204, *Physical Properties of Optical Materials* (in press).
- ⁴C. F. Cline and M. J. Weber, "Beryllium Fluoride Optical Glasses: Preparation and Properties," *Wiss. Ztschr. Friedrich-Schiller-Univ. Jena, Math.-Nat. R.*, 28, Jg. H. 2/3, 351 (1979); also available as Lawrence Livermore Laboratory Rpt. UCRL-81168.
- ⁵K. H. Sun, "Fluoride Glasses," *Glass Technology* 20, 36 (1979).
- ⁶H. Rawson, *Inorganic Glass-Forming Systems* (Academic Press, London and New York, 1967).
- ⁷M. J. Weber, D. Milam, and W. L. Smith, "Nonlinear Refractive Index of Glasses and Crystals," *Opt. Engin.* 17, 463 (1978).
- ⁸N. L. Boling, A. J. Glass, and A. Owyong, "Empirical Relationships for Predicting Nonlinear Refractive Index Changes in Optical Solids," *IEEE J. Quantum Electron.* QE-14, 601 (1978).
- ⁹D. Heiman, R. W. Hellwarth, and D. S. Hamilton, "Raman Scattering and Nonlinear Refractive Index Measurements of Optical Glasses," *J. Non-Cryst. Solids* 34, 63 (1979).
- ¹⁰R. W. Hellwarth, "Third-Order Optical Susceptibilities of Liquids and Solids," in *Progress in Quantum Electronics*, Vol. 5 (Pergamon Press, London, 1977).
- ¹¹S. H. Wemple, "Optical Oscillator Strengths and Excitation Energies in Solids, Liquids, and Molecules," *J. Chem. Phys.* 67, 2151 (1977).
- ¹²W. L. Smith, "Laser-Induced Breakdown in Optical Materials," *Opt. Engin.* 17, 489 (1978).
- ¹³J. R. Bettis, A. H. Guenther, and R. A. House II, "Refractive-Index Dependence of Pulsed-Laser-Induced Damage," *Optics Lett.* 4, 256 (1979).

- ¹⁴B. E. Newman and D. H. Gill, "Ultraviolet Damage Resistance of Laser Coatings," NBS Spec. Publ. 541, *Laser Induced Damage in Optical Materials: 1978*, p. 190.
- ¹⁵J. 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, 510-523 (1979).
- ¹⁶See, for example, V. I. Nikitin, M. S. Soskin, and A. I. Khizhnyak, "Influence of uncorrelated inhomogeneous broadening of the 1.06 μ band of the Nd³⁺ ions on laser properties of neodymium glasses," *Sov. J. Quantum Electron.* 8, 788 (1978).
- ¹⁷A. Brawer and M. J. Weber, "Observation of Fluorescence Line Narrowing, Hole Burning, and Ion-Ion Energy Transfer in Neodymium Laser Glass," *Appl. Phys. Lett.* 35, 31-33 (1979).
- ¹⁸J. Hegarty and W. M. Yen, "Optical Homogeneous Linewidths of Pr³⁺ in BeF₂ and GeS₂ Glasses," *Phys. Rev. Lett.* 43, 1126 (1979).
- ¹⁹J. M. Pellegrino, J. Hegarty, W. M. Yen, and M. J. Weber, "Composition Dependence of Nd³⁺ Homogeneous Linewidth in Glasses," *Bull. Amer. Phys. Soc.* 25, 419 (1980).
- ²⁰W. H. Dumbaugh and D. W. Morgan (private communication).
- ²¹S. E. Stokowski, D. Milam, and M. J. Weber, "Laser Induced Damage in Fluoride Glasses: A Status Report," in NBS Spec. Publ. 541, *Laser Induced Damage in Optical Materials: 1978*, p. 99.
- ²²F. 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).

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.