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## RECENT DEVELOPMENTS IN LASER GLASSES

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The past decade has witnessed a proliferation of new glass-forming compositions including oxides, halides, oxyhalides, and chalcogenides. Many of these glasses are applicable to lasers and have greatly expanded the range of optical properties and spectroscopic parameters available to the laser designer. Our knowledge and understanding of many properties of interest for laser action--transparency, linear and nonlinear refractive indices, and damage threshold of the host glass and the absorption spectrum, radiative and nonradiative transition probabilities, fluorescence wavelength, stimulated emission cross section, and spectroscopic inhomogeneities of the lasing ion  $\text{Nd}^{3+}$ --are reviewed.

### Introduction

In the first decade after the birth of the laser in 1960, many different glasses were investigated as possible laser ion hosts.<sup>1,2</sup> These were principally oxide glasses, however a few halides and mixed glass formers were also investigated.<sup>3,4</sup> In the 1970s, the glass requirements for specific laser systems, such as large Nd:glass lasers for inertial confinement fusion research<sup>5,6</sup> and miniature lasers for integrated optics,<sup>7,8</sup> prompted a renewed search for improved glass compositions. Concurrently, the past decade has witnessed the discovery of many new halide glasses based on compounds not previously considered as glass progenitors.<sup>9</sup> These developments have combined to expand the range of optical and spectroscopic parameters available to the laser designer. In addition, systematic studies of glass properties as a function of composition have shown how many of them can be tailored to optimize performance.<sup>10,11</sup>

In this brief survey, a number of the optical and spectroscopic properties of oxide, nonoxide, and mixed anion glasses are compared. Properties of interest for laser applications include the transparency of the host glass at the optical pumping and lasing wavelengths and the ability to store and extract energy from the lasing ion. In the latter category, specific limiting properties include:

#### Energy Storage

- Absorption spectrum
- Excited state lifetimes
- Quantum efficiency

#### Energy Extraction

- Stimulated emission cross section
- Inhomogeneous spectroscopic properties
- Nonlinear refractive index
- Laser-induced damage

For some properties, information sufficient to comment about relative advantages of different glass types already exists; for others, little or no data is available and additional studies are needed before the relative merits can be established. Since many glasses have only been melted in small research quantities, the methods and costs associated with producing large quantities of high optical quality glass are unknown. The category of unknowns for new glasses may also include chemical durability, mechanical and fabrication properties, thermo-optic properties, solarization, ...

All glass lasers to date have used a rare earth as the active ion and optical pumping for excitation.<sup>12</sup> Of these, flashlamp-pumped  $\text{Nd}^{3+}$  lasers are by far the most used and studied glass lasers. Because of the associated large data base, we restrict the comparison of spectroscopic properties to those of  $\text{Nd}^{3+}$ . Many of the conclusions and trends, however, are also applicable to other rare earth ions.

The spectroscopic data was obtained from small ( $\sim 1 \text{ cm}^3$ ) samples. Based on the resulting parameters and computer models, it is possible to estimate the relative laser performance in both the small-signal<sup>13</sup> and large-signal<sup>14</sup> gain regimes. Thus many different glasses can be surveyed and predictions made without actually demonstrating laser action.

### Glass Compositions

The number of new glass forming systems reported in recent years is large and still growing. Although most developments have been in the area of nonoxide glasses, the range of oxide glasses also continues to expand (see, e.g., Ref. 15). It is not possible to review this rapidly proliferating subject in detail here. Instead, examples of several nonoxide glasses are listed in Table I.<sup>16-27</sup> While beryllium fluoride glasses have been

known for over fifty years, most of the other glasses in Table I have been reported within the past decade. The extent of the glass forming regions for these multicomponent glasses vary widely; a representative composition of each is given but the reference cited should be consulted for information about the range of compositions and physical properties possible.

In addition to multicomponent glasses containing a single anion species, glasses exist containing a mixture of anions. For example, glasses can be formed with compositions ranging from phosphates with a few mole percent fluoride to mixed fluoride glasses with a few mole percent phosphate. Several examples of mixed anion glasses are given in Table II.<sup>28-35</sup> Since the anion is the lasing ion ligand, it has a large effect on determining the spectroscopic properties. In mixed anion glasses there may also be mixed anion nearest-neighbor coordination. This introduces an additional degree of local disorder into an already disordered structure and increases the inhomogeneity of the spectroscopic properties of the lasing ion.<sup>36</sup> The probability of having mixed anion coordination has been discussed in terms of the theory of hard and soft acids and bases.<sup>11</sup>

It is evident from the glass compositions in Tables I and II and the many known oxide glass forming systems<sup>37</sup> that, depending on the chemical composition of the host glass, the local fields at a laser ion site may vary greatly. The glasses included in these tables are, in many cases, those in which  $\text{Nd}^{3+}$  has been added to investigate how changes in local field affect spectroscopic properties and laser parameters. The only glasses in these lists for which actual laser action has been studied extensively are the fluoroberyllates.<sup>16,38</sup>

Table I. Examples of nonoxide glasses.

Glass type	Representative composition (molt)	Reference
<b>Fluorides</b>		
Beryllium fluoride	$60\text{BeF}_2\text{-}20\text{KF-}10\text{CaF}_2\text{-}10\text{AlF}_3$	16
Cadmium fluoride	$30\text{CdF}_2\text{-}40\text{BaF}_2\text{-}30\text{ZnF}_2$	17
Lead fluoride	$50\text{PbF}_2\text{-}25\text{MnF}_2\text{-}25\text{GaF}_3$	18
Aluminum fluoride	$45\text{AlF}_3\text{-}35\text{CaF}_2\text{-}20\text{BaF}_2$	19
Zirconium fluoride	$62\text{ZrF}_4\text{-}33\text{BaF}_2\text{-}5\text{LaF}_3$	20
Hafnium fluoride	$62\text{HfF}_4\text{-}23\text{BaF}_2\text{-}10\text{LaF}_3$	21
Thorium fluoride	$40\text{ThF}_4\text{-}20\text{BaF}_2\text{-}30\text{YbF}_3$	22
<b>Chlorides</b>		
Bismuth chloride	$60\text{BiCl}_3\text{-}40\text{KCl}$	23
Thorium chloride	$40\text{ThCl}_4\text{-}30\text{NaCl-}30\text{KCl}$	24
<b>Bromide</b>		
Bismuth bromide	$70\text{BiBr}_3\text{-}20\text{TlCl-}10\text{PbCl}_2$	25
<b>Sulfides</b>		
Aluminum sulfide	$75\text{Al}_2\text{S}_3\text{-}25\text{La}_2\text{S}_3$	26
Gallium sulfide	$70\text{Ga}_2\text{S}_3\text{-}30\text{La}_2\text{S}_3$	27

Table II. Examples of mixed anion glasses.

Glass type	Representative composition (molt)	Reference
<b>Halides</b>		
Chloride-iodide	$50\text{ZnCl-}50\text{KI}$	28
Bromide-chloride	$60\text{BiBr}_3\text{-}25\text{TlCl-}15\text{PbCl}_2$	25
<b>Oxyhalides</b>		
Phosphate-fluoride	$5\text{Al}(\text{PO}_3)_3\text{-}12\text{M}^{\text{I}}\text{F-}51\text{M}^{\text{II}}\text{F}_2\text{-}32\text{AlF}_3$	29
Phosphate-chloride	$35\text{P}_2\text{O}_5\text{-}35\text{Na}_2\text{O-}30\text{ZnCl}_2$	30
Zirconia-fluoride	$40\text{ZrO}_2\text{-}20\text{LiPF}_6\text{-}40\text{KPF}_6$	31
Tellurite-chloride	$66\text{TeO}_2\text{-}11\text{BaO-}23\text{ZnCl}_2$	32
Sulfate-chloride	$40\text{Na}_2\text{SO}_4\text{-}60\text{ZnCl}_2$	28
<b>Oxysulfides</b>		
Silicate-sulfide	$75\text{SiO}_2\text{-}25\text{Na}_2\text{S}$	33
Gallium-lanthanum	$70\text{Ga}_2\text{S}_3\text{-}30\text{La}_2\text{O}_2\text{S}$	34
<b>Oxynitride</b>		35
	$\text{Y}_2\text{O}_3\text{-AlN-SiO}_2$	

### Transparency

The transparency of the host glass is important for both energy storage and energy extraction: for the former at optical pumping wavelengths, for the latter at stimulated emission wavelengths. Although oxide glasses are known that transmit from approximately 0.2 to 9  $\mu\text{m}$ ,<sup>15</sup> the short- and long-wavelength extremes are both exceeded by halide glasses. The glasses with the largest fundamental band gaps are those based on beryllium fluorides,<sup>39</sup> where transmission below 150  $\mu\text{m}$  has been reported.<sup>40</sup> Therefore fluoroberyllate glasses are potential hosts for UV and VUV laser action, for example involving  $5d \rightarrow 4f$  emission of rare earths.<sup>41</sup>

At long wavelengths the transparency of halide glasses is again better than that of oxide glasses. This has led to the consideration of halide glasses for low-loss optical fiber materials.<sup>42,43</sup> The infrared absorption edge of glass is governed by multiphonon processes and depends on the glass composition.<sup>44,45</sup> Several heavy metal fluoride glasses transmit well in the 5-10  $\mu\text{m}$  region. Chloride glasses have recently been reported that transmit out to 13  $\mu\text{m}$  ( $\text{ThCl}_4$ )<sup>24</sup> and 14  $\mu\text{m}$  ( $\text{BiCl}_3$ ).<sup>23</sup> Although the sulfide glasses in Tables I and II transmit from about 0.5 to 10  $\mu\text{m}$ , other chalcogenide glasses transmit beyond 15  $\mu\text{m}$ , but with reduced visible transmission.<sup>26</sup>

To date no solid-state paramagnetic ion laser has operated beyond 5  $\mu\text{m}$ ; in glass the longest wavelength laser action is only 2  $\mu\text{m}$ .<sup>12</sup> Efficient laser action becomes more difficult to achieve at longer wavelengths because the probability for radiative transitions from excited electronic states decreases at the same time that the probability for nonradiative transitions by multiphonon emission increases.<sup>47,48</sup> Hence halide and chalcogenide glasses with low vibrational cutoff frequencies offer the combined advantages of greater infrared transparency and reduced decay by nonradiative processes, thereby extending the wavelength range of possible stimulated emission.

### Absorption Spectra

Absorption spectra of trivalent rare earths vary with the glass forming and glass modifying ions. Whereas the  $4f$  energy levels exhibit only small shifts with host composition, spectral intensities and effective linewidths exhibit greater variations. Optical pumping of rare-earth glass lasers is usually done using Xe flashlamps. Their emission spectrum consists of a quasi-blackbody continuum in the visible with line spectra in the near-infrared. The relative pumping efficiency of different Nd-doped glasses is determined by combining the flashlamp spectrum with the glass absorption spectrum.<sup>13</sup> Studies of pumping efficiencies for many different oxide and halide glasses<sup>49</sup> show that the variations with composition are not large, usually <50%.

During optical pumping, ions accumulating in the upper laser level can also absorb pump radiation. The resulting excitation to higher lying levels and subsequent decay to the upper laser level or other levels constitutes a loss which may be significant when excited-state populations become large. The probability of excited-state absorption can be estimated from the radiative intensity parameters.

### Radiative Intensity Parameters

The optical transitions of rare earths in solids are predominantly of electric dipole character and their spectral intensities can be described using the treatment of Judd and Ofelt.<sup>50</sup> In this approach the line strength  $S$  of a transition between two  $J$  states is given by a sum of products of empirical intensity parameters  $\Omega_t$  and matrix elements of tensor operators  $U^{(t)}$  of the form

$$S(J, J') = \sum_{t=2,4,6} \Omega_t \left| \langle \alpha J U^{(t)} \parallel \alpha J' \rangle \right|^2. \quad (1)$$

The values of  $\Omega_t$  are obtained from a least-squares fit of measured and calculated absorption line strengths and typically have an experimental uncertainty of  $\sim 10\%$ . The integrated intensities of the absorption bands yield  $\Omega$ 's which are an effective average over the different rare earth environments in the glass.

The most significant factor determining the  $\Omega$  values is the strength of the odd-order terms in the expansion of the local field at the rare earth site. These, in turn, are affected by the nearest-neighbor anion(s) and cations. For a given glass former, systematic changes of  $\Omega_t$  have been observed with changes in the size and charge of network modifier ions.<sup>49,51-55</sup>

The  $\text{Nd}^{3+}$  intensity parameters have been determined for hundreds of oxide and nonoxide glass compositions; the ranges of values observed are summarized in Table III. In the cases of silicate, phosphate, and fluoroberyllate glasses, a large compositional space was explored; for other glasses only a few or a single composition were examined. Therefore the values in Table III are representative but may not be the extreme values possible.

The  $\Omega$ 's for the oxide glasses are all of comparable magnitudes. The most significant differences with respect to the halide glasses are the small values of  $\Omega_2$  for the

Table III. Range of Judd-Ofelt intensity parameters for Nd<sup>3+</sup> in different glass types.

Intensity parameter	$\Omega_2(\text{pm}^2)$	$\Omega_4(\text{pm}^2)$	$\Omega_6(\text{pm}^2)$	Reference
<b>Oxides</b>				
Silicate	2.4-7.0	1.7-5.1	1.8-5.9	49,51
Germanate	3.6-5.9	3.3-4.8	2.9-5.4	49
Tellurite	3.0-5.7	2.9-5.1	3.4-5.0	49,53
Phosphate	2.9-6.7	3.3-6.0	3.8-6.8	49,54
Borate	3.2-4.7	3.3-4.7	4.3-6.1	49
<b>Halides</b>				
Fluoroberyllate	0.1-1.7	2.5-5.6	3.2-6.1	49,52
Fluorozirconate	1.8-2.0	3.6-3.8	4.1-4.4	20
Fluorohafnate	1.3	3.6	3.6	49
Fluoroaluminate	0.6-2.4	3.2-4.2	4.1-4.9	49
Chloride	2.2-5.7	6.6-8.1	4.4-5.0	11
<b>Oxyhalides</b>				
Fluorophosphate	1.3-4.7	3.2-5.6	3.5-6.4	49
Chlorophosphate	2.4-3.5	5.4-5.9	6.2-6.6	55
<b>Chalcogenides</b>				
Sulfide	6.6-9.4	4.4-6.8	3.9-6.5	26,34
Oxysulfide	8.2	3.4	3.9	34

fluorides and the large values of  $\Omega_4$  for the chlorides. The  $\Omega$  values for the mixed anion fluorophosphate glasses are intermediate to those for pure phosphate and pure fluoride glasses. Chalcogenide glasses, because of their more covalent bonds, have large  $\Omega$  values.

The intensity parameters enter into calculations of radiative transitions between any 4f<sup>n</sup> states of interest. These include ground-state absorption, excited-state absorption, and spontaneous and stimulated emission. The radiative lifetime  $\tau_R$  of the <sup>4</sup>F<sub>3/2</sub> state of Nd<sup>3+</sup> is calculated from the  $\Omega_4$  and  $\Omega_6$ . The behavior of the intensity parameters with composition can therefore be used to predict changes in several important laser parameters.

#### Stimulated Emission Cross Section

The rate of energy extraction from a laser material is dependent on the stimulated emission cross section which is given by

$$\sigma = \frac{8\pi^3 e^2}{3hc(2J+1)} \frac{(n^2 + 2)^2}{n} \frac{\lambda_p}{\Delta\lambda_{\text{eff}}} S(J, J') \quad (2)$$

where  $n$  is the refractive index,  $\lambda_p$  is the wavelength of the emission peak and  $\Delta\lambda_{\text{eff}}$  is the effective linewidth of the emission between states  $J$  and  $J'$ . Since the emission bands of rare earths in glass are usually asymmetric and consist of inhomogeneously broadened transitions between several Stark levels, an effective linewidth<sup>50</sup> obtained by integrating over the band and dividing by the peak intensity is used in Eq. (2).

Of the quantities determining  $\sigma$  in Eq. (2),  $S$ ,  $\Delta\lambda_{\text{eff}}$ , and  $n$  are strongly host dependent. The variation of  $S$  is governed by the combination of  $\Omega_i$ 's that enter into Eq. (1) and their change with glass composition noted earlier. The rare-earth ligands have the greatest influence on the linewidth. In general, the smaller the anionic field strength, the smaller the Stark splitting and the narrower the effective linewidth. Therefore  $\Delta\lambda_{\text{eff}}$  is narrowed by using monovalent halide rather than divalent oxide anions. Among different glass-forming systems, the narrowest linewidths appear when the rare earth can establish the most asymmetric, chemically uniform coordination sphere possible. This occurs when the rare earth does not have to compete with the glass-forming cations for the available ligands. Finally, for a given glass network former,  $\Delta\lambda_{\text{eff}}$  generally increases with increasing charge and decreasing size of the modifying cations.<sup>38</sup> These rules and the increase of  $\sigma$  with  $n$ ,<sup>53</sup> have been used to tailor stimulated emission cross sections.<sup>11</sup>

The ranges of effective stimulated emission cross sections for the <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> transition of Nd<sup>3+</sup> observed for different glass types are summarized in Table IV together with associated ranges for  $n$ ,  $\Delta\lambda_{\text{eff}}$ ,  $\lambda_p$  and  $\tau_R$  (values cited are again not necessarily the extreme values possible). The ranges of cross sections are also depicted in Fig. 1. For silicate glasses,  $\sigma$  varies by a factor of 4 by changing the host composition from an alkali silicate to a high-refractive-index bismuth silicate. The peak cross sections obtainable for phosphates

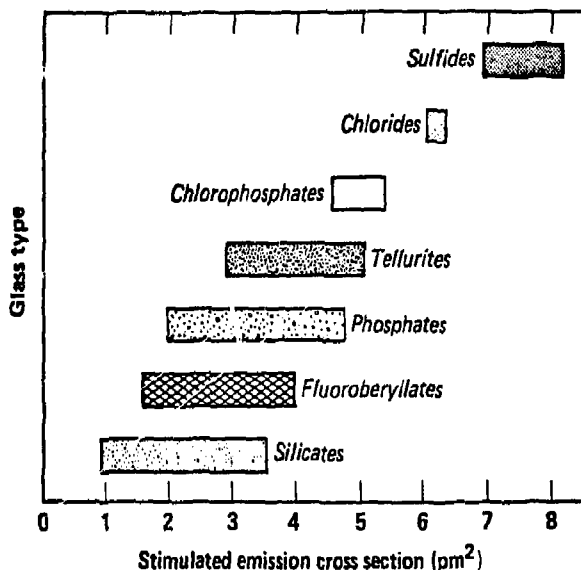


Figure 1. Ranges of peak stimulated emission cross sections reported for the  $^4F_{3/2} \rightarrow ^4I_{11/2}$  transition of  $\text{Nd}^{3+}$  in glasses at 295 K.

are larger than for silicates. This is not because the line strengths ( $\Omega_t$ ) are significantly larger but because the  $\Delta\lambda_{\text{eff}}$  are narrower. Some tellurite glasses have even larger  $\sigma$ 's than for phosphates, not because S or  $\Delta\lambda_{\text{eff}}$  are more favorable but because of their large  $n$  values.

As expected, the halide glasses have narrower linewidths than the narrowest oxide glass (phosphates) in Table IV. For the fluoroberyllate glasses, this does not result in larger cross sections than for phosphate glasses because the  $\Omega_t$  are smaller. Chloride glasses combine a small  $\Delta\lambda_{\text{eff}}$  with larger  $\Omega_t$  and a high refractive index to yield stimulated emission cross sections larger than those for any oxide glass. The high-index, near linewidth, covalently-bonded chalcogenide glasses result in the largest  $\text{Nd}^{3+}$  cross sections observed thus far.

#### Spectroscopic Inhomogeneities

Differences in local environments of rare earths in glass cause site to site variations in energy levels and transition probabilities. The cross sections and lifetimes noted above are actually effective averages over an ensemble of physically different sites. In the small-signal gain regime where the signal grows exponentially, these average values are sufficient to model laser performance. However, in the large-signal gain regime where a major fraction of the stored energy is extracted, preferential de-excitation of ions with large cross sections leads to significantly different saturation behavior than that predicted from average values.<sup>14</sup> The energy extraction efficiency of two lasing media with the same initial small-signal gain, one of which is spectroscopically homogeneous and the other inhomogeneous, will always be less for the latter.

A distribution of stimulated emission cross sections exists in a glass because of differences in the energy levels, natural (homogeneous) linewidths, and line strengths.<sup>57</sup> This results in spectral and polarization hole burning phenomena under large-signal or saturated gain laser operation. To predict this behavior, the distribution of  $\sigma$  values for radiation of a given frequency and polarization is needed. Although complete, unambiguous data of this type is not available, useful information about spectroscopic inhomogeneities can be obtained from a combination of standard optical spectroscopy and laser-induced fluorescence line-narrowing (FLN) techniques.<sup>57</sup> These measurements yield information about homogeneous and inhomogeneous linewidths,  $\Delta\nu_h$  and  $\Delta\nu_{ih}$ , and the average anisotropy of the stimulated emission cross section for light polarized parallel (p) or perpendicular (s) to the major axis as the site. Using these results, large variations in extraction efficiency of short-pulse glass laser amplifiers are predicted as a function of  $\Delta\nu_h/\Delta\nu_{ih}$  and  $\sigma_p/\sigma_s$ .<sup>58</sup>

To date there have only been limited measurements of the spectroscopic inhomogeneities needed to compare the relative advantages of oxide versus halide laser glasses in the large-signal regime. Studies have shown large (factor of  $\approx 3$ ) variations in both  $\Delta\nu_h$  and  $\Delta\nu_{ih}$  as a function of glass composition.<sup>59</sup> Resonant polarized FLN experiments demonstrate that

the cross sections of individual sites are not isotropic, therefore the effect of random site orientation must be considered when using polarized laser beams.<sup>60</sup> Actual amplifier gain measurements show that phosphate glasses saturate more homogeneously than fluorophosphate and silica glasses.<sup>61</sup> These studies combine to demonstrate that significant variations in saturation behavior are possible, however systematic investigations of a large range of glass types are needed to guide the development of the best glasses for saturated gain operation.

### Nonlinear Optical Properties

In high-power glass lasers,<sup>6</sup> the beam intensities  $I$  may become so large that they induce changes in the optical properties of the amplifier glass and all transmitting optical components. The intensity-dependent refractive index is given by

$$n = n_0 + n_2 I + \dots \quad (3)$$

where  $n_2$  is the nonlinear refractive index coefficient. Although the induced index change  $n_2 I$  is small (typically ppm), for large laser systems the resulting whole-beam and small-scale self-focusing can lead to significant losses in focusable energy on target.

Self-focusing effects are minimized by using low- $n_2$  glasses.<sup>62</sup> Although accurate calculations of  $n_2$  are not possible, empirical relationships for  $n_2$  in terms of  $n$  and the Abbe number  $\nu$  have been derived<sup>63</sup> from measured  $n_2$  values for a large number of different oxide and halide glasses and crystals.<sup>64</sup> Lines of constant  $n_2$  appropriate for the long-wavelength limit, that is, wavelengths far removed from the fundamental absorption edge, are plotted on a  $n$ - $\nu$  diagram in Fig. 2 together with regions of known optical glasses. A large reduction in  $n_2$  is achieved by using low-index, low-dispersion glasses in the lower left-hand corner of Fig. 2. The location of the different glass types in this figure can be obtained from the refractive index values in Table IV.

When the laser photon energy becomes equal to or greater than one-half of the band gap energy  $E_g$ , two-photon absorption becomes energetically possible. This intensity-dependent loss is given by the coefficient  $\beta$  in the expression

$$\frac{dI}{dz} = -\alpha I - \beta I^2 - \dots \quad (4)$$

Two-photon-induced solarization has also been observed in optical glasses. In addition, the nonlinear refractive index increases as the laser wavelength approaches a two-photon absorption, thereby increasing the effects of self-focusing.

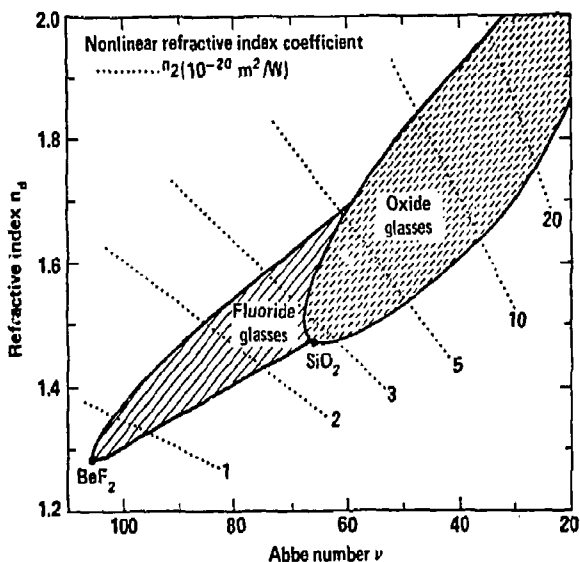


Figure 2. Refractive index and Abbe number for optical glasses. Dashed lines of constant nonlinear refractive index  $n_2$  at long wavelengths are calculated from expressions in Ref. 63.

Table IV. Range of spectroscopic properties for the  $^4F_{3/2} \rightarrow ^4I_{11/2}$  transition of  $\text{Nd}^{3+}$  in different glasses at 295 K.

Glass	$n_d$	Cross section $\sigma(\text{pm}^2)$	Wavelength $\lambda_p(\text{nm})$	Linewidth $\Delta\lambda_{\text{eff}}(\text{nm})$	Lifetime $\tau_R(\mu\text{s})$	Ref.
<b>Oxides</b>						
Silicate	1.46-1.75	0.9-3.6	1057-1088	34-55	170-1090	49,51
Germanate	1.61-1.71	1.7-2.5	1060-1063	36-43	300-460	49
Tellurite	2.0-2.1	3.0-5.1	1056-1063	26-31	140-240	49,53
Phosphate	1.49-1.63	2.0-4.8	1052-1057	22-35	280-530	49,54
Borate	1.51-1.69	2.1-3.2	1054-1062	34-38	270-450	49
<b>Halides</b>						
Fluoroberyllate	1.28-1.38	1.6-4.0	1046-1050	19-29	460-1030	49,52
Fluorozirconate	1.52-1.56	2.9-3.0	1049	26-27	430-450	20
Fluorohafnate	1.51	2.6	1048	26	520	49
Fluoroaluminate	1.41-1.48	2.2-2.9	1049-1051	30-33	420-570	49
Chloride	1.67-2.06	6.0-6.3	106201064	19-20	180-220	11
<b>Oxyhalides</b>						
Fluorophosphate	1.41-1.56	2.2-4.3	1049-1056	27-34	310-570	49
Chlorophosphate	1.51-1.55	5.2-5.4	1055	22-23	290-300	56
<b>Chalogenides</b>						
Sulfide	2.1-2.5	6.9-8.2	1075-1077	21-22	64-100	26,34
Oxyulfide	2.4	4.2	1075	27	92	34

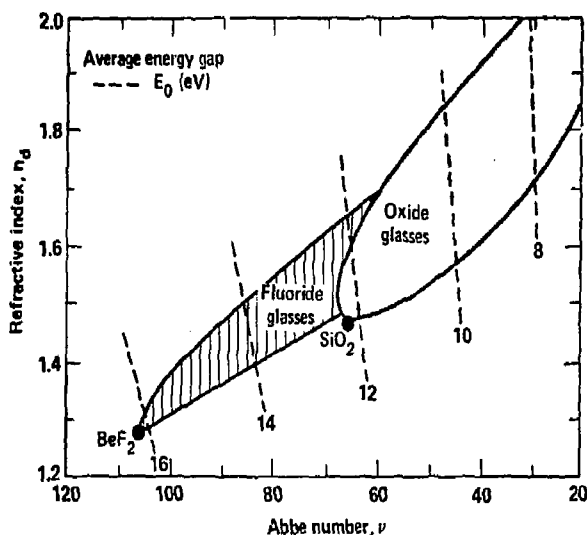


Figure 3. Refractive index and Abbe number for optical glasses. The dashed lines are plots of an average energy gap  $E_0$  for a single effective dispersion oscillator (see Ref. 39). The optical absorption edge is approximately  $2/3-3/4$  of  $E_0$ .

All of the above effects are minimized by using wide band gap glasses. A rough estimate of the average energy gap can be obtained from index dispersion data. The results plotted as lines of constant effective  $E_0$  in an  $n-v$  diagram<sup>39</sup> are shown in Fig. 3. Beryllium fluoride and aluminum fluoride-based glasses with small atomic number modifier cations have the widest band gaps and smallest optical nonlinearities. The optical nonlinearities of oxide glasses are reduced by replacing O by F, as for example in fluorophosphate and fluorosilicate



glasses; the resulting  $n_2$  values of these glasses are comparable to those of the heavier metal (Zr, Hf) fluoride glasses. Oxide glasses with high-atomic-number modifiers, the heavier halide glasses, and chalcogenide glasses are generally unattractive for high-power laser applications where  $n_2$  is an important consideration.

#### Laser-Induced Damage

The rate of energy extraction from a laser is ultimately limited by the maximum intensity per unit area that can be propagated without damage to the glass. Damage may occur either in the bulk, due for example to metallic particles (Pt) and other imperfections,<sup>65</sup> or at the surface due to associated physical or chemical defects.<sup>66</sup> The dominant source of damage is frequently dependent on the manufacturing process, but for high quality optical glasses the threshold for surface damage is generally lower than that of the bulk. Variations in damage thresholds of diverse transparent materials are frequently not large, suggesting that their origin may be extrinsic rather than intrinsic.

Laser-induced damage thresholds for surfaces and thin films exhibit a systematic increase with decreasing refractive index.<sup>67</sup> In addition, the surface damage threshold at the exit surface is lower than at the entrance surface by the ratio  $[(n+1)/2n]^2$ , which again favors low-index glasses.

#### Conclusions

The preceding brief survey of optical and spectroscopic properties of oxide and nonoxide glasses demonstrates that an increasingly wider range of glass parameters are becoming available to the laser designer. In comparing different glasses, the largest property variations are obtained by changing the glass former; changing the glass modifiers produces additional but usually smaller variations. Because of the large number of compositional possibilities, generalizations attributing specific characteristics to a given glass type must be used carefully. For example, although phosphate glasses have large stimulated emission cross sections, silicate glasses exist with larger cross sections than some phosphate.

Which glass is best for a specific laser application depends on the requirements for wavelength, pulse duration, spectrum and duration of the pump source, small- or large-signal operation, and optical configuration. The size of the glass components and their environment impose questions of production and chemical durability. Although a glass may have the best overall laser characteristics, cost and availability are the final arbiters in the selection process.

Two areas where additional work is needed to establish the relative merits of various glasses for lasers are (1) measurements of spectroscopic inhomogeneities and their effects on large-signal energy extraction and (2) investigations of laser-induced damage thresholds as a function of wavelength and pulse duration for a wider range of glass compositions.

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