A unified materials approach to mitigating optical nonlinearities in optical fiber. III. Canonical examples and materials road map

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Abstract  
This paper, Part III in the Trilogy (Ballato, Cavillon, Dragic, 2018; Dragic, Cavillon, Ballato, et al., 2018a,b), provides a road map for the development of simple core/clad optical fibers whose enhanced performance—in particular, marked reductions in optical nonlinearities—is achieved materially and not through the more conventional present routes of geometrically complex fiber design. More specifically, the material properties that give rise to Brillouin, Raman and Rayleigh scattering, transverse mode instabilities (TMI), and \( n_2 \)-mediated nonlinear effects are compiled and results on a wide range of optical fibers are discussed with a focus on trends in performance with glass composition. Furthermore, optical power scaling estimations as well as binary and ternary property diagrams associated with Rayleigh scattering, the Brillouin gain coefficient (BGC) and the thermo-optic coefficient \( (dn/dT) \) are developed and employed to graphically represent general trends with composition along with compositional targets for a single intrinsically low nonlinearity, silica-based optical fiber that can achieve the power scaling goals of future high energy fiber laser applications. A foundational finding of this work is that the high-silica content optical fibers fabricated using conventional chemical vapor deposition methods will not suffice to meet the power scaling demands of future high-power and high-energy fiber lasers.

KEYWORDS  
glass products, lasers, optical fibers, optical glasses, optical properties

1 | INTRODUCTION

This trilogy of papers generally is focused on mitigating the optical nonlinearities that arise when high optical powers are propagated through modern optical fibers. These nonlinearities, which include stimulated Brillouin scattering (SBS), stimulated Raman scattering (SRS), transverse mode instability (TMI), and nonlinear refractive index \( (n_2) \)-mediated wave-mixing phenomena, are parasitic effects in that they limit the achievable output powers from fiber lasers. While the fiber and laser community has largely confronted these issues through tailoring of the fiber geometry, this work lays the foundation for a unified materials approach. The benefits of which are that each nonlinearity is attacked at its most fundamental origin—the interaction of the light with the material through which it propagates—and, accordingly, simpler fiber designs and ease of manufacturing result.

Companion Paper ¹ provided a fundamental description of the thermodynamical and physical origins of each effect
along with the general dependencies of each on material properties and parameters. Companion Papers II discussed simple macroscopic additivity models that have proved quite useful for estimating the relevant optical, acoustic, thermal, and physical properties of multicomponent glasses. The intent of this paper is to build from the fundamentals of Companion Paper I and describe the properties of specific glass families as they relate to the aforementioned performance-limiting optical nonlinearities.

By way of a compositional baseline, modern telecommunications optical fibers possess a pure silica cladding with a germania (GeO₂)-doped single-mode core. The use of germania originates from its processibility using chemical vapor deposition (CVD) methods to yield extremely low loss fibers. High energy laser (HEL) fibers, and to some extent erbium-doped fiber amplifier (EDFA) fibers, replace the GeO₂ with combinations of alumina (Al₂O₃) and phosphorus pentoxide (P₂O₅), in order to limit photo-darkening, along with facilitating the incorporation of the appropriate rare-earth species (typically either Er₂O₃ or Yb₂O₃). Other species, such as SiF₄ or boria (B₂O₃) are added to further tailor the refractive index, viscosity, or stress state in the glass. A summary of the role of each of these dopants on the resulting glass can be found in Refs. 4, 5. Complementing this discussion is the nice comparison of preform fabrication methods for silicate fibers that is found in Ref. 5.

Ideally, the compositions discussed herein would be realized using conventional CVD methods. However, given the high processing temperatures associated with preform consolidation and collapse, which usually exceed 2200°C (and are often closer to 2400°C), volatile species such as germania (GeO₂), boria (B₂O₃), and fluorine (F) are difficult to maintain in the necessary concentrations required for marked reduction in parasitic nonlinearities. In this sense, the molten core approach to fiber fabrication, employed to make many of the fibers discussed in this work, can be considered a “low temperature” method since the highest temperature experienced is approximately the melting point of the core precursor. This can be several hundreds of degrees lower than those experienced in CVD processing, which permits greater concentrations of the more volatile species to persist in the final fiber. However, while convenient and amenable to a wide range of materials, the reaction between core melt and cladding glass can make achieving low-silica core compositions a challenge. Additionally, the attenuation from molten core-derived all-glass fibers is predicated on the purity of the starting materials, which usually are powder-derived. While sub-20 dB/km loss values have been obtained, this is presently more the exception than the rule without significant purification efforts.

Accordingly, the following ground rules have been considered from the perspective of practicality. First, whether for telecommunications or HEL applications, fibers must be robust, spliceable to existing (silica) fibers, capable of reasonable rare-earth doping levels, and low loss (20-30 dB/km for HEL laser fibers although less is always better). “Robust,” in these cases, refers to their fieldability, which requires high strength, flexibility, and reasonably high temperature capacity (HEL fibers can experience temperatures of several hundred degrees Celsius during operation). As waveguides, the modality of the fiber is important from the perspective of dispersion (telecommunications) and beam quality (HEL). In the former, single-mode operation generally is required, whereas in the latter, single-mode operation would be preferred but multi-mode operation might suffice. When considering all of these attributes together, particularly with hopes of operation at > kW optical power levels, only silica-based optical fibers fulfill these conditions.

In specific regard to the nonlinearities themselves, this work assumes the following reductions to be both practical and viable. Practical here means that achieving these levels of reduction would be meaningful from a HEL systems perspective: −15 dB in Brillouin gain coefficient (BGC); −5 dB in Raman scattering; a thermo-optic coefficient (dn/dT) of −5 dB; and an n² value equivalent to that of pure SiO₂. While the last goal does not sound like an improvement, achieving the other reductions will necessitate reasonably high concentrations of non-SiO₂ compounds. Accordingly, this n² goal essentially means that these non-SiO₂ dopants would not have any additional contribution to the nonlinear refractive index beyond that of the SiO₂ component.

2 | TRENDS WITH GLASS COMPONENTS AND FAMILIES

The properties of multicomponent glass optical fibers were studied in detail in the 1970s and 1980s while efforts to optimize optical fibers for long-haul communications were being undertaken with great enthusiasm. In those days, low optical loss was the principal driver and so compositions that exhibited intrinsically low Rayleigh scattering garnered the most attention. Seminal material examples of such fibers will now be described as a preamble to the discussions that follow.

Among the first studies were those conducted on the classic soda-lime-silica (SLS) system. An analysis similar to that provided in Companion Paper I was conducted, although focused primarily on losses associated with Rayleigh scattering. Due to the reduced fictive temperature, the density-related Rayleigh scattering was predicted to be lower for the SLS than for fused silica. However, additional scattering due to compositional fluctuations in the multicomponent SLS glass led to a calculated intrinsic loss that was slightly over three times larger than that for silica across the visible and near infrared spectral range (extrinsic impurities notwithstanding).
Contemporaneously, the binary potassium silicate system was studied with both Rayleigh and Brillouin scattering being investigated as a function of $K_2O$ concentration. With increasing $K_2O$, both $p_{12}$ and $p_{44}$ photoelasticity coefficients, shear and longitudinal wave velocities, and fictive temperature were found to decrease. Conversely, the refractive index and isothermal compressibility were shown to increase with increasing $K_2O$ concentration. These trends were shown by LaBerge et al., to yield density fluctuations, $\langle \Delta p^2 \rangle$, that were nearly 50% lower than those for SiO$_2$ at a concentration of about 20 mol% $K_2O$. However, Schroeder et al. found that the immiscibility gap that exists in the $K_2O$-SiO$_2$ system, which extends over the range from nominally 0-25 mol% $K_2O$, led to significant compositional fluctuation-induced scattering. For $K_2O$ concentrations greater than 25 mol%, the scattering losses were found to be roughly 30% lower than for fused silica due primarily to the very small compositional fluctuation term associated with Rayleigh scattering. Taken in total, potassium silicates are intrinsically low Brillouin and Rayleigh glasses for $K_2O$ concentrations in excess of 20-25 mol%. Again, it is worth noting that extrinsic losses associated with impurities likely would make this system impractical from the perspective of low loss telecommunication fibers. However, given the differing focus of this present trilogy, where ultimate low loss is not as critical, such a simple system with intrinsically low Brillouin and (classical) Rayleigh scattering could be of interest.

Ternary silicate glasses also received considerable attention, particularly those in the sodium borosilicate (Na$_2$O-B$_2$O$_3$-SiO$_2$) and sodium aluminosilicate (Na$_2$O-Al$_2$O$_3$-SiO$_2$) systems. As noted by Tynes et al., a glass system that exhibits both refractive index and density values that are roughly independent of composition must then exhibit a $\partial \rho / \partial C$ value of zero (or nearly so), which implies low Rayleigh scattering. Akin to the concept employed here of component additivity to achieve multiple property tailoring, Tynes et al., further postulated that a ternary borosilicate with low total Rayleigh scattering could be achieved by mixing a binary borosilicate (B$_2$O$_3$-SiO$_2$) having reduced $\rho$ with a binary alkali silicate exhibiting a reduced $\langle \Delta p^2 \rangle$ value (see Companion Paper I for more detail on these factors). These conditions occur over a fairly broad compositional range in the sodium borosilicate system, where, for a composition of about 50 SiO$_2$-20 B$_2$O$_3$-30 Na$_2$O (mol%) a minimum in Rayleigh scattering occurs due to the aforementioned combined effects of reduced density fluctuations and reduced change in permittivity (hence refractive index) with density. A similar approach was followed in the sodium aluminosilicate system, where Rayleigh scattering was reduced through reductions in fictive temperature to minimize density fluctuations coupled with components well-matched in dielectric properties to minimize compositional fluctuations. A composition of 78 SiO$_2$-6 Al$_2$O$_3$-16 Na$_2$O (mol%) was found to exhibit scattering losses 60% lower than fused silica.

Quaternary systems also have been studied with the mixed alkali, alkaline earth silicate system being especially interesting. Specifically, Tsujikawa and Ohashi evaluated glasses in the $K_2O$-Na$_2O$-MgO-SiO$_2$ system. They found a marked reduction in Rayleigh scattering for a composition of 22 $K_2O$-8 $Na_2O$-10 MgO-60 SiO$_2$ (mol%) where the scattering losses are only about 38% those for fused silica. For this composition, the combined effects at play are a reduced glass transition temperature (surrogate for fictive temperature), hence reduced density-related scattering, as well as the reduced concentration fluctuations postulated to arise from a maximum at this composition in the difference between the glass transition and spinodal temperatures. This later consideration being thought to occur based on the mixed alkali effect, whereby the mobility of the faster diffusing alkali species exhibits a minimum at a ratio of $K_2O/(K_2O + Na_2O)$ of about 0.73.

A more general and systematic consideration of alkali ion effects in silica-based optical fiber glasses was made by Lines. Shown there were changes in fictive temperature, $T_f$, refractive index, $n$, photoelastic constant $p_{12}$, and difference between glass transition and spinodal temperatures, $(T_g-T_s)$, with small (<4 mol%) alkali addition into silica. Of the alkali ions, sodium and potassium silicates were found to have the lowest overall scattering loss, relative to the other alkali, due primarily to their having the greatest reduction in $T_f$, larger $T_g-T_s$ difference (particularly for $K_2O$-SiO$_2$), and smallest increase in refractive index. A minimum in scattering was found at a concentration of about 2 mol% alkali with the sodium and potassium silicates exhibiting a calculated Rayleigh scattering that was 15-20% lower than for fused silica. These dependencies, however, in some part derive from the formation of non-bridging oxygen (NBO) ions upon alkali addition into silica. Such defects will not be helpful at higher intensities in active optical fibers because they are believed to facilitate photo-darkening. However, this is set aside for the time being in the present discussion.

For completeness, it is noted that in all of these aforementioned cases, only the cationic species are changed. The influence of fluorine addition was studied by Lines in the alkali silicate system. Fluorine is known to reduce the refractive index and, when added into glass with small alkali concentrations, it was found also to decrease $\rho$. For fluorine concentrations up to 2 wt% (N.B., weight percent; not mole percent as previously employed), the total attenuation of low alkali content (fluoro)silicate was shown to be reduced by 15-20% relative to fused silica. This is instructive since, below, examples will be provided on multicomponent
oxyfluoride glasses that are used to further tailor Raman scattering and the nonlinear refractive index, $n_2$.

The point of this section has not been to provide an exhaustive literature survey of multicomponent glasses for low loss optical fibers. Instead it has been to offer a few examples of how simple, well known and studied glass systems, offer opportunities for reducing what are today the performance-limiting parasitic effects in some of the most advanced optical fiber laser and communication systems.

Table 1 provides the general trends in selected properties of interest to this work with the addition of said dopants into SiO$_2$. As can be seen, in each case, compounds can be found that either increase or decrease a given property, and so the consideration here is to identify those compounds that suitably reduce each or, preferably, several nonlinearities, while forming a homogeneous core glass that meets the aforementioned practicality conditions; this is no simple task. Where no trend (arrow) is given, the direction of the change with said compound into silica has not yet been determined.

### Table 1 General property trends on addition of noted compound into silica

| Compound  | Physical$^b$ | BRILLOUIN$^b$ | STRS$^b$ | Raman$^b$ | Wave-Mixing$^b$ |
|-----------|--------------|--------------|----------|----------|-----------------|
|           | $n$ | $\rho$ | CTE | $V_a$ | $\Delta V_B$ | $p_{12}$ | $dn/dT$ | $V_m$ | $n_2$ |
| SiO$_2$   | 1.444 | 2200 | $0.55 \times 10^{-6}$ | 5970 | 17 | 0.226 | 10.4 | 27.31 | 2.5 | $10^{-20}$ |
| GeO$_2$   | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| F         | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ |
| P$_2$O$_5$| ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| B$_2$O$_3$| ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ |
| Al$_2$O$_3$| ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| Yb$_2$O$_3$| ↑↑ | ↑↑ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ |
| La$_2$O$_3$| ↑↑ | ↑↑ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ |
| Lu$_2$O$_3$| ↑↑ | ↑↑ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ | ↓↓ |
| MgO       | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| CaO       | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| SrO       | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| BaO       | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| Li$_2$O   | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| Na$_2$O   | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| K$_2$O    | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| Y$_3$Al$_5$O$_{12}$ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |

$^a$Trend strictly valid over homogeneous glass-forming range and for the binary composition with silica. Ternary and $n$-ary glasses may show equivalent trends but will depend on the relative concentrations of each component. Additionally, trends presume that no new phase or structure is formed such as with the mixed alkali effect$^{61,62}$ or in the Al$_2$O$_3$-P$_2$O$_5$ system where both Al$_2$O$_3$ and P$_2$O$_5$ increase the refractive index, for example, when individually added to silica but decrease it when both Al$_2$O$_3$ and P$_2$O$_5$ are added in equal proportions to silica due to the formation of AlPO$_4$.63

$^b$Property abbreviations and units: $n$ is the linear refractive index [dimensionless], $\rho$ is the density [kg/m$^3$], CTE is the coefficient of thermal expansion [K$^{-1}$]. $V_a$ is the acoustic velocity [m/s], $\Delta V_B$ is the Brillouin linewidth [MHz], $p_{12}$ is the transverse photoelastic coefficient [dimensionless], $dn/dT$ is the thermo-optic coefficient [K$^{-1}$]. $V_m$ is the molar volume (cm$^3$/mol), and $n_2$ is the nonlinear refractive index (m$^2$/W).

$^c$Values for silica: refractive index, $n$, measured at a wavelength of 1550 nm. Brillouin linewidth, $\Delta V_B$, measured in MHz at a Brillouin frequency of 11 GHz.

### 3 COMPOSITIONAL EFFECT ON INDIVIDUAL OPTICAL NONLINEARITIES

As noted above, it is infeasible to thoroughly review the impact of each possible compound on all of the material properties that influence the parasitic nonlinearities discussed in this trilogy. Accordingly, this section discusses compositional effects of a few compounds and compound families that have been shown to influence each nonlinearity in the manner desired. Section 5 then takes these individual considerations and brings them together into a common set of exemplar fibers.

#### 3.1 Brillouin scattering

As detailed in Companion Paper I,1 spontaneous Brillouin scattering materially depends on the refractive index, transverse photoelastic coefficient, and adiabatic compressibility. In its stimulated form (SBS), the Brillouin gain coefficient, BGC, is materially dependent upon the Brillouin linewidth, $\Delta V_B$, the acoustic velocity, $V_a$, and the molar volume, $V_m$.
$\Delta v_B$, (which is inversely proportional to the phonon lifetime) in addition to the factors noted above. Accordingly, to determine the magnitude of Brillouin scattering or, for the more specific purposes of these works, the BGC, one needs either to directly measure or accurately deduce the following material properties: refractive index, $p_{12}$ photoelasticity, density, acoustic wave velocities, and Brillouin spectral width.

Considerable literature exists detailing compositional effects on refractive index and density. To a lesser extent, photoelasticity and acoustic wave velocities (hence, elastic constants and, therefore, adiabatic compressibility values) are known as are, to an even lesser extent, Brillouin spectral widths. Furthermore, care should be taken when citing photoelastic coefficients from the literature since many conventional methods for their determination measure magnitude but not sign, the latter being quite critical here.

Figure 1 provides an overlay of the Brillouin gain coefficient, relative to a conventional telecommunications optical fiber, as a function of non-SiO$_2$ content of the core glass composition. More specifically, it depicts $\text{BGC}_{\text{log}} = 10 \log_{10} (\text{BGC}_{\text{core}} / \text{BGC}_{\text{SMF-28}})$ where the BGCs in the operand are in units of m/W. Consequently, where the BGC goes to zero, the graph takes on a singularity that extends to $-\infty$ on the vertical scale. This composition is referred to as Zero Brillouin Activity, or ZeBrA. Figure 1 is equivalent to Figure 6 in Companion Paper IIB, which employs data from Table 1 in Companion Paper IIB, except that experimental values are overlaid here as the open color-coded circles to show the fit between measurements and modeling. For completeness, the compositional dependencies in Figure 1 and Figure 6 in Companion Paper IIB on the $p_{12}$ photoelasticity values are those from Figure 5 in Companion Paper IIA, remembering that the Brillouin gain coefficient is proportional to $p_{12}$.

From the perspective of specific glass systems to be employed for the reduction of Brillouin scattering, several features of interest are observed in Figure 1. The first, and perhaps most obvious features are the minima that are shown for selected binary and ternary silicates; particularly for alkaline earth silicates (e.g., barium and strontium silicates) and sesquioxide silicates (e.g., aluminosilicates and lanthanum aluminosilicates). As noted in Companion Paper I, the $p_{12}$ photoelasticity has the potential to take on a value of zero and, under such conditions, Brillouin scattering then goes to zero. It is further worth noting that, despite the possibility to completely eradicate an otherwise fundamental physical phenomenon, a reduction in BGC of >15 dB is sufficient for the present and foreseeable future fiber-based systems. If one focuses instead on the −15 dB points for each curve, and not these singular ZeBrA points, then considerable compositional ranges exhibiting this reduction exist.

A second feature is that the (modeled) curve associated with the YAG-derived yttrium aluminosilicate (Y$_2$O$_3$-Al$_2$O$_3$-SiO$_2$) fiber does not show such a BGC$_{\text{log}} \to -\infty$ minima while the (modeled) curve for lanthanum aluminosilicate (SiO$_2$-Al$_2$O$_3$-La$_2$O$_3$; SAL) does. In the yttrium aluminosilicate fiber, single crystalline YAG (Y$_3$Al$_5$O$_{12}$) was employed as the core precursor during the molten core fabrication. In the lanthanum aluminosilicate fiber, a homogenous SAL glass rod was first made and then employed as the core phase in a rod-in-tube fiber draw arrangement. In conducting the modeling, per those methods outlined in Companion Paper IIB, the measured data fit both systems best when the properties of crystalline YAG were employed in the former case and the properties of a mixture of La$_2$O$_3$ and Al$_2$O$_3$ were used in the latter. Since homogeneous crystalline YAG possesses a small but positive $p_{12}$ value, when mixed with the $p_{12} > 0$ SiO$_2$ ($p_{12} = 0.226$ at a wavelength of 1550 nm for fused silica), there is no composition where the resultant “YAG-derived” silicate glass would show a BGC$_{\text{log}} \to -\infty$ feature.

For the SAL fiber, the measured Brillouin gain data fit best when the individual La$_2$O$_3$ and Al$_2$O$_3$ components, along with SiO$_2$, were used. Based on the known properties of fused silica, along with previously additivity-
deduced properties of the Al$_2$O$_3$ component from measurements on aluminosilicate glasses, contributions from the La$_2$O$_3$ components also can be deduced and are shown in Table 1 in Companion Paper IIB.\textsuperscript{3} Based on the $p_{12} < 0$ values deduced for Al$_2$O$_3$ and La$_2$O$_3$, the resultant (modeled) curve exhibits the $p_{12} = 0$ minima. This clearly is a point for continued study: other than being the source of the individual components, what other roles might the form (crystal vs glass, homogeneous vs heterogeneous powder) of the precursor play in the properties of the final glass fiber? For completeness, the compositions achieved are not especially near the ZeBrAl compositions for either of these glasses and so perhaps the argument is moot and one simply cannot extrapolate property trends over the entire range of compositions. Over what range of compositions then can property values be extrapolated is another question for the continued study.

As a brief aside, it is of direct benefit to the amplifier and laser fibers that these sesquioxides lower the Brillouin gain coefficient when added into silica. Sesquioxide Al$_2$O$_3$ is added to silica in order to reduce the thermodynamic tendency for rare-earth dopant clustering. Such clustering diminishes the quantum efficiency of the light emission.\textsuperscript{20–22} Accordingly, the typical dopants employed for making active silica-based optical fibers are intrinsically low Brillouin materials, although, in most applications, their concentrations are fairly low (few weight percent) and so the effect is less obvious.

In conclusion, with respect to this section, while the conventional dopants into SiO$_2$ that are employed in communication optical fibers do lower the Brillouin gain coefficient (Figure 6 in Companion Paper IIB\textsuperscript{3}), markedly lower BGC values are possible when compounds possessing negative $p_{12}$ values are incorporated into silica, whose $p_{12}$ is positive. This “mean value theorem” additivity yields $p_{12} = 0$ compositions that could, if realized in practice, negate Brillouin scattering. As will be discussed in more detail below, dopants of choice for reduced Brillouin scattering are the alkaline earth oxides, (AE)O, specifically SrO and BaO. They possess the most negative $p_{12}$ values deduced to date and have miscibility limits in SiO$_2$ of 42 and 40 mol%, respectively,\textsuperscript{23} although subsolidus metastable immiscibility is known.\textsuperscript{24} The inclusion of 5-10 mol% Al$_2$O$_3$ has proven an effective approach to mitigating phase separation at high (AE)O concentrations should glass formation be problematic\textsuperscript{25}; see the \textit{(Classical)} Rayleigh Scattering section.

\section*{3.2 | Raman scattering}

In both its spontaneous and stimulated forms, Raman scattering is reduced for glasses comprised of compounds possessing low molar volume, $V_m$, and small bond compressibility parameters, $\Lambda$; specifically, $P_{Raman} \propto V_m \cdot \Lambda^2$. As two points of reference: (a) in the well-studied alkali halide system, $\Lambda$ decreases with both increasing cationic ($\Lambda_{Li} > \Lambda_{Na} > \Lambda_K > \Lambda_Rb$ for a given halide) and anionic ($\Lambda_F > \Lambda_CL > \Lambda_Br > \Lambda_I$ for a given cation) mass\textsuperscript{26–28} and (b) of greater relevance here, $\Lambda$ for SiO$_2$ is quite small (0.1) and tends to increase with increasing modifier content.\textsuperscript{15,29} Given the few tangible material parameters that directly influence Raman scattering and, for those factors, the scarcity of available data on their magnitude as a function of composition, Figure 2 provides a meager compilation of results from more common glass systems. The data employed in Figure 2 is either directly provided or computed from Refs. 27,30–32 and the fractional cationic concentrations were calculated per Lines.\textsuperscript{29}

While the bond compressibility parameter is not as directly measurable as is, for example, the photoelastic coefficient(s), as noted in Companion Paper I, $\Lambda$ does take on positive and negative values depending on the molecular structure and polarizability of the compound at hand. Thus, at least in theory, $\Lambda = 0$ ($\Lambda^2 = 0$) glasses could be

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{The product $V_m \times \Lambda^2$ (molar volume and squared bond compressibility parameter), which is proportional to the total Raman scattering intensity,\textsuperscript{1,29} as a function of non-silica cationic fraction for a series of binary and ternary oxide glasses.\textsuperscript{30} Lines connecting data within each glass family are guides-to-the-eye. SiO$_2$ is included as a point of reference [Color figure can be viewed at wileyonlinelibrary.com]}
\end{figure}
possible. However, as with all nonlinearities, diminution is of greater practical consequence than eradication.

Figure 3 provides a compilation of measured relative peak Raman scattering values for a variety of fibers studied for their intrinsically low optical nonlinearities. The Raman scattering data shown in Figure 3 were obtained as discussed in Companion Paper II using a normalization procedure similar to that in Ref. 33.

Care should be taken in comparing the results of Figures 2 and 3. As noted, Figure 2 is comparing the bond compressibility and molar volume, which are proportional to the total Raman scattering intensity. Figure 3 is comparing the Raman gain coefficient, which is proportional to the peak Raman intensity suitably normalized. If 2 molecules scatter with equivalent (spontaneous) Raman strength, but 1 molecule has twice the spectral bandwidth (or twice as many spectral components), then it will exhibit half the peak Raman gain coefficient.

Additionally, the Raman response is dependent both on the polarizability of the species, the overlap of each species’ Raman spectral components, and the degree of disorder in the glass structure. For example, as discussed in Ref. 34, relative to yttrium aluminosilicate glasses, the molten core-derived core possessed broader SiO₂-related Raman spectral features than the pure SiO₂ cladding, implying a more random molecular structure. Additionally, there is little overlap between the Raman peaks of the individual components in these multicomponent glasses. As a result, both the peak SiO₂ scattering intensity is reduced by virtue of a lower silica content in the resultant glass, and the broader distribution of Raman spectral features yields a reduced intensity at any given wave-number. These “structural” factors are not accounted for in the theories that yielded Figure 2 and suggest that the glass structure (and fiber draw processing) may be more deterministic in measured Raman scattering intensity for a given family of glasses.

Interestingly, \( \Lambda \) also factors into laser damage thresholds; a separate but still important factor in the practicality of the HEL fibers considered in this trilogy. More specifically, \( \Lambda \), which formally is defined as \( \Lambda = -\frac{\delta n}{\delta p} = (1 - \Lambda) \frac{\delta n}{\delta p} \), can be evaluated through the relationship: \( \rho \frac{\delta n}{\delta p} = (1 - \Lambda) \rho \frac{\delta n}{\delta p} \). As noted by Waxler, a material with zero \( \frac{\delta n}{\delta p} \) value (or \( \Lambda = 1 \)) would exhibit no electrostrictive effects, including laser damage or (electrostrictive) self-focusing.\(^{36,37}\) Perhaps the more important lesson here is that, fundamentally, there are only a handful of material parameters/coefficients that relate to most (optical) phenomena; for example, Table 2 in Companion Paper I.\(^1\) It is in this simplicity that the sophistication of a unified materials approach to reducing nonlinearities originates.

Lastly, and for completeness, although not shown in Figure 3, conventional telecommunication dopants, namely GeO₂, B₂O₃, and P₂O₅, all possess larger Raman scattering cross sections than SiO₂.\(^{38}\) More specifically, the relative Raman cross sections are about 5, 6, and 9 times larger for B₂O₃, P₂O₅, and GeO₂ than for SiO₂, respectively.\(^{38}\) Furthermore, GeO₂ is well known to increase the nonlinear refractive index, \( n_2 \), of silicate glasses;\(^{39}\) see Figure 4 in Companion Paper II.\(^3\) Accordingly, for the purposes of this Trilogy, these dopants will not be considered other than to provide baseline comparisons for the intrinsically low nonlinearity glasses discussed later against conventional optical fiber core compositions.

### 3.3 | (Classical) Rayleigh scattering

As relates to HEL fibers, losses are not as critical as in long-haul communication fibers since path lengths are markedly shorter than for telecomm fibers. For example, an oceanic fiber cable can extend several thousand kilometers, whereas an amplifier or laser fiber typically is 10-20 m in length. This is not to say that loss is irrelevant, lower losses are always preferred. However, the attenuation of telecommunication fibers is specified as being \(<0.2\ \text{dB/km}\), whereas for laser fiber’s, the attenuation is typically \(<10-20\ \text{dB/km}\).

From Companion Paper I,\(^1\) it is known that 2 contributions to Rayleigh scattering exist in optical fibers; those relating to fluctuations in concentration (composition) and in density. Materially, the intensity associated with concentration-related scattering is linearly proportional to the...
fictive temperature, quadratically proportional to the change in dielectric constant with composition (\(\varepsilon_k\)), and inversely proportional to the change in chemical potential with composition. The chemical potential approximately scales inversely with the difference between the fictive and spinodal temperatures.\(^1\,31\) Accordingly, for large (\(T_s-T_f\)), one prefers then a system with no immiscibility or, for those that do, lower \(T_s\) values are better.

From the perspective of specific systems, as noted in Companion Paper I,\(^1\) a glass system that possesses both refractive index and density values that are roughly independent of composition should exhibit intrinsically low Rayleigh scattering. As an example, binary borosilicates (\(B_2O_3-SiO_2\)) possess reduced \(\varepsilon_k\) values, whereas binary alkali silicates exhibit reduced \(\langle \Delta p^2 \rangle\) values.\(^12\) Accordingly, the sodium borosilicate system is particularly interesting because it exhibits reduced Rayleigh scattering due to these combined effects.

With respect to increasing (\(T_s-T_f\)), one approach would be the addition of alumina, which is known to aid in glass formation by shifting the upper consolute point to lower temperatures.\(^21\) In other words, relative to a composition without \(Al_2O_3\), an alumina-containing glass will exhibit phase separation at a larger degree of undercooling, where kinetics are slower and such instability is therefore less likely. Accordingly, in a system containing \(Al_2O_3\), (\(T_s-T_f\)) would be larger, which suggests that Rayleigh scattering should be reduced; all other properties being equal. Another approach to increasing (\(T_s-T_f\)) is to use an isostuctural additive that reduces the upper consolute point relative to that compound it is replacing.\(^10\)

Contributions to Raleigh scattering associated with density fluctuations are materially dependent on the refractive index, \(n\), the fictive temperature, \(T_f\), the photoelasticity coefficient, \(p\) [\(p = p_{12} + (2/3)p_{44}\)], and the adiabatic compressibility, \(K_S\), through the elastic stiffnesses.\(^1\) Of these dependencies, the trend with refractive index is most pronounced, scaling as \(n^8\), followed by that with photoelasticity, scaling as \(p^3\), and then linearly with \(T_f\) and \(K_S\).

From the perspective of specific glass systems, the same compounds discussed above with respect to reduced Brillouin scattering are useful here for reducing the \(p_{12}\) contribution to photoelastic influences on Rayleigh scattering. In the limiting case of a \(p_{12} = 0\) zero Brillouin Activity “\(ZeBrA\)” composition, only the \(p_{44}\) contribution would remain as a photoelastic contributor for Rayleigh scattering. Taken from the other perspective, \(p_{44}\) glasses have not only been identified but have been realized\(^{40,41}\) Representative glasses include those in the \(SnO-B_2O_3\), \(SnO-P_2O_5\), \(SnO-SiO_2\), \(PbO-B_2O_3\), \(PbO-P_2O_5\), and \(PbO-SiO_2\) families.\(^41\,42\) Unfortunately, these glasses all exhibit high refractive indices and low melting points making them unlikely candidates for the silica-clad fibers preferred in this Trilogy. That said, they do represent excellent systems through which to study the underlying correlations between glass chemistry and structure and optical physics.

Figure 4 provides the photoelastic properties of these glasses, along with those for silica and selected commercial glasses and crystals.\(^10,26,27,31,41,43–45\) As a general trend, the oxide glasses tend to exhibit larger \(p_{12}\) values than do halide crystals. Furthermore, PbO-based glasses, including the SF6 dense flint glass, possess near-zero \(p_{44}\) values. Of particular interest is YAG, which has both \(p_{12}\) and \(p_{44}\) values quite near to the \(p = 0\) line. Accordingly, YAG-derived yttrium aluminosilicate glasses might be of interest for intrinsically low Rayleigh scattering optical fibers.

As noted in Table 1 of Companion Paper I,\(^1\) the density-related component of Rayleigh scattering would go to zero for a glass possessing a zero hydrostatic photoelasticity value, \(p = 0\). This is analogous to the \(p_{12} = 0\) “\(ZeBrA\)” condition for Brillouin scattering previously mentioned. Accordingly, Figure 4 also displays the \(p = p_{12} + (2/3)p_{44} = 0\) line. Assuming equivalent additivity of \(p\) to that of \(p_{12}\) discussed in Companion Paper IIA,\(^2\) Section 4 that follows will discuss potential \(p = 0\) compositions that would negate this contribution to Rayleigh scattering. As noted in Companion Paper I,\(^1\) while Rayleigh is not a limitation in high-power laser systems, any scattering may contribute to other stimulated processes or, more generally, loss. Thus, any diminution in scattering is generally of benefit.

### 3.4 Transverse mode instability (TMI)

As noted in Companion Paper I,\(^1\) transverse mode instability is widely believed to be associated with stimulated thermal Rayleigh scattering (STRS). From a materials perspective, per Dong,\(^46\) TMI-related mode coupling via STRS is proportional to the thermo-optic coefficient (shortened to TOC or \(dn/dT\) in the text) and inversely proportional to the product of density with heat capacity.

From this, two important considerations arise as relates to this Trilogy. First is that, over the range of glass compositions from which practical HEL fibers are made, neither the density nor heat capacity (or thermal conductivity\(^47\)) change very much.\(^48\) The second, and perhaps more important consideration, is that the thermo-optic coefficient has the potential to take on a value of zero; see, for example, Figure 2 of Companion Paper IIB.\(^3\) In an analogous manner to which \(p_{12} = 0\) negates Brillouin scattering, \(dn/dT = 0\) would negate STRS, although, again, negating such physical properties are not always needed in practice as long as sufficient reductions are achieved. Accordingly, for the purposes of this work, dopants into silica that yield reductions in the thermo-optic coefficient, such as \(B_2O_3\) and \(P_2O_5\) (or, at least, do not dramatically raise \(dn/dT\) values, such as the alkaline earth oxides) will be considered further.
4 | PROPERTY VALUE COMPOSITIONAL DIAGRAMS

The underlying goals of this Trilogy are to explicate the fundamental physical origins of performance-limiting nonlinear phenomena in optical fibers, determine or deduce their material dependencies, and identify glass families and compositions that collectively reduce all of the parasitic effects. In other words, to create a path to the compositions that collectively reduce all of the parasitic nonlinearities in optical fibers, determine or deduce their material dependencies, and identify glass families and compositions that collectively reduce all of the parasitic nonlinearities in optical fibers.

Prior activities investigating the effect of various dopants have largely focused on binary systems for reasons of simplicity in trying to understand the underlying factors at play. Examples of how the nonlinearities scale with composition of single additives into SiO$_2$ can be found in Figure 2 above, for the Brillouin gain coefficient (BGC), and in Figure 2 in Companion Paper IIB, for the thermooptic coefficient that drives TMI. Since no single additive is likely to reduce all of the parasitic nonlinearities to the levels desired, more complex multicomponent systems need to be studied and their influences understood.

Figure 4 shows that the Pockels coefficient, $p = p_{12} + (2/3)p_{44}$. Also shown are lines representing a zero Pockels coefficient material, where Rayleigh scattering would be zero. Data taken from the References noted [Color figure can be viewed at wileyonlinelibrary.com] for a variety of glasses, glass families, and crystals (measured at a wavelength of 632 nm). Rayleigh scattering scales quadratically with $p$ and decreases from silica. Also shown are lines representing a zero Pockels coefficient material, where Rayleigh scattering would be zero. Data taken from the References noted [Color figure can be viewed at wileyonlinelibrary.com]

Exemplifying this is Figure 5, which represents the dependence of TOC/$p$ (heat capacity not considered since it changes very little with composition) for three canonical glass families treated in this Trilogy. Values deduced using the additivity models presented in Companion Paper IIA and, in the particular case of the TOC, values do not take into account thermal expansion mismatches with the cladding. Of note here, as expected based on the $dn/dT = 0$ potential in the B$_2$O$_3$-SiO$_2$ and P$_2$O$_5$-SiO$_2$ systems, such zero STRS glasses are identified and will be further discussed in Section 4.

- SiO$_2$: Glass formation, thermal and mechanical stability, high laser damage threshold, compatibility with existing fibers and global manufacturing processes. SiO$_2$ also exhibits a very low Raman cross section and nonlinear refractive index.

Needs Attention: Additives to reduce $p_{12}$ and $dn/dT$ (see below).

- Al$_2$O$_3$: Facilitates glass formation, hence lowers $T_s$, which reduces Rayleigh scattering; and has (slightly) negative $p_{12}$ value. Its large longitudinal acoustic velocity can be used to make a fiber acoustically antiguiding and decrease the phonon lifetime (broaden $\Delta v_B$). It is also known to reduce photo-darkening, and can allow greater introduction of active rare-earth ions relative to silica.

Needs Attention: Additive for reduction in $dn/dT$.

- BaO or SrO: Strongly negative $p_{12}$ value to reduce Brillouin and density-related Rayleigh scattering; although would likely contribute to stronger Raman scattering and wave-mixing given the higher molar volume, (likely) bond compressibility, and polarizability of these heavy metal oxides. However, when added to silica in fairly low proportion (up to 10-15 mol%), it reduces the magnitude of the Raman gain.

Needs Attention: Additives to reduce $dn/dT$.

- P$_2$O$_5$: Negative $dn/dT$ values, which, when incorporated into silica ($dn/dT > 0$), offer potential to negate STRS,
hence greatly reduce TMI. P$_2$O$_5$ facilitates reduced photo-darkening.

- B$_2$O$_3$: Glasses containing B$_2$O$_3$ typically exhibit lower density, linear and nonlinear refractive indices, negative $dn/dT$ value; and significantly increases Brillouin linewidth.

Needs Attention: Both B$_2$O$_3$ and P$_2$O$_5$ greatly increase Raman gain relative to silica, but only a small addition may be beneficial such as for alkaline earth oxides. Furthermore, effect of B$_2$O$_3$ on photo-darkening has not yet been determined.

- Alkali oxides: Lowers $T_f$ and facilitates glass formation, which reduces Rayleigh scattering. Unfortunately, beyond Li$_2$O, insufficient data exist from which to deduce all of the properties of interest here, so these glasses, including alkali boro- and aluminosilicates, will not be discussed, but clearly represent areas for further study. That said, there is considerable reason to further investigate their role in reducing parasitic optical nonlinearities given their known potential for reducing Rayleigh scattering at small concentrations.15,16

The property value ternary diagrams treated next do not include fluorine or fluorides. This is because, to date, the exact bonding of the fluorine in the multicomponent silicate systems investigated has not been determined. Since, therefore, the exact compound composition cannot be determined, then neither can properties be deduced based on the additivity procedures of Companion Paper II. That said, the following compounds, and related oxyfluoride glasses, are worthy of further consideration.

- F: Reduces linear ($n$) and nonlinear ($n_2$) refractive indices; reduces Raman scattering and increases tendency for binary systems to phase separate/devitrify.50
- Alkaline earth fluorides: Reduces $n$, $n_2$, $dn/dT$, and, likely, Raman scattering.
- Rare-earth fluorides: Rare-earth ions make the glass light emissive while the fluorine contributes to off-setting the index-raising qualities of the rare-earth.

4.1 Caveats

The section that follows begins by providing property value representations for selected ternary and quaternary glass systems based on the compounds noted above. Specifically, compositional trends in the transverse photelastic coefficient, $p_{12}$, the hydrostatic photelastic coefficient, $p$, and the thermo-optic coefficient [(dn/dT), TOC]. These coefficients are chosen because they materially influence Brillouin scattering, density-related Rayleigh scattering, and stimulated thermal Rayleigh scattering, which mediates TMI. Furthermore, among the material parameters that factor into each parasitic nonlinearity, these are the ones that change most with composition and, most importantly, they have the potential to take on values of zero.

Compositional representations for Raman scattering and nonlinear wave-mixing will not be provided since, at present, there are insufficient data available on the governing material properties (specifically $\Lambda$ and $n_2$) to deduce compositional trends. However, as shown in Paper IIB,3 when those properties are known (eg, GeO$_2$), the additivity approaches seem to offer sufficient accuracy for the purposes of this work in identifying glass families and compositional ranges for intrinsically low nonlinearity optical fibers.

SiO$_2$ is employed as a base constituent in all cases considered in this Section for reasons of practicality; specifically that silicate core compositions would be most compatible with an SiO$_2$ cladding that would yield high strength, potentially low loss, and integration with conventional fibers to which these fibers would be spliced; for example, pump couplers. That said, as long as attenuation levels were suitably low and strength were to be sufficient, there is no practical reason why a core/clad preform with desired NA and dimensions could not be fashioned and drawn using these multicomponent glasses directly.

Lastly, the diagrams that follow cover the entire ternary compositional regions and are not limited to specific glass-forming regions. The reasoning for this is 3-fold: (i) their purpose is to show global compositional trends; (ii) the glass-forming “limits” are not well known for all of these systems; and (iii) glass-forming is kinetically enabled and dependent on the glass (or fiber) forming method. It is
known that, for example, the molten core approach enables fiber compositions that are not possible using conventional melting/casting or optical fiber chemical vapor depositions methods.\textsuperscript{4,51} Hence, future efforts and approaches may continue to open up the compositional space over which glass optical fibers can be achieved.

Prior to delving into each nonlinearity individually (and then collectively), Figure 6 provides a representative example for the Brillouin gain coefficient, BGC in the SrO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} system. The associated Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} and SrO-SiO\textsubscript{2} BGC binaries are overlaid to illustrate the complementary nature of this graphical approach. As expected, although Zero Brillouin Activity (ZeBrA) occurs at a single composition in a binary system, it occurs over a range of compositions in a ternary system. In addition to providing a simple graphical representation of compositional dependence on the parasitic nonlinearities, this approach also provides a simple way to visualize wide ranges of compositions that meet selected criteria, such as a $-30$ dB suppression in Brillouin gain coefficient relative to a conventional fiber, which is shown as the dashed lines connecting the binaries to the associated edges of the ternary in Figure 6.

### 4.2 | Intrinsically low (classical) Rayleigh scattering glasses

As a brief reminder, Rayleigh scattering arises from fluctuations in both composition and density.\textsuperscript{1} Admittedly, compositional contributions are more difficult to estimate given unknown additivity/deduction of fictive temperatures and chemical potential. As such, just the contributions associated with density will be considered in this Section. That said, while both the refractive index and isothermal compressibility (through the elastic constants) can be estimated, only the photoelasticity ($p$) will be discussed as it, of the material factors influencing Rayleigh scattering, has the most reasonable potential to take on a value of zero or, at least, be significantly reduced.

Based on deduction of the photoelasticity as described in Companion Paper IIA,\textsuperscript{2} Figure 7 provides property value diagrams for hydrostatic photoelasticity coefficient, $p = p_{12} + (2/3)p_{44}$, for selected compositional families for the compounds noted above. In the glass systems commonly employed in telecommunication fibers (GeO\textsubscript{2}, P\textsubscript{2}O\textsubscript{5}, and B\textsubscript{2}O\textsubscript{3}), there are no markedly interesting effects to employ. The inclusion of Al\textsubscript{2}O\textsubscript{3}, however, begins to drive reductions in aggregate $p$ values due to its low photoelasticity. This is further exemplified with alkaline earth oxide dopants, notably SrO and BaO, whereby $p = 0$ compositions can be identified. At these compositions, density contributions to Rayleigh scattering should be zero and marked reductions in the overall Rayleigh scattering should be significant. Again, as noted in Companion Paper I,\textsuperscript{1} while Rayleigh scattering is not, per se, a parasitic nonlinearity as relates to high energy fiber lasers, it can seed other stimulated processes. Furthermore, it contributes to the fiber’s base attenuation. Accordingly, any reduction of Rayleigh scattering is beneficial.

### 4.3 | Intrinsically low transverse mode instability glasses

Mode instabilities in “effectively single mode” large mode area optical fibers are driven by thermo-optic effects associated with stimulated thermal Rayleigh scattering (STRS). As noted in Companion Paper I, STRS is distinct from the “classical” Rayleigh scattering just treated.\textsuperscript{1} Based on the additivity approaches of Companion Paper IIA,\textsuperscript{2} the deduced thermo-optic coefficients for the glass families treated herein are provided in Figure 8.

With respect to conventional telecommunication dopants, P\textsubscript{2}O\textsubscript{5} and B\textsubscript{2}O\textsubscript{3} possess negative $dn/dT$ values, whereas GeO\textsubscript{2} and SiO\textsubscript{2} possess positive ones. Accordingly, compositions exhibiting intrinsically low thermo-optic effects can be realized using conventional fiber materials and processes, although compatibility with index profiles and modality may be challenging. Of the additional dopants identified in this Triloxy, the alkaline earth oxides again show intriguing opportunities for low and possibly zero $dn/dT$ values at high SiO\textsubscript{2} concentrations. For completeness, it is worth noting that one would normally expect SrO and BaO to behave somewhat similarly. The differences in compositional thermo-optic trends shown in Figure 8 between the SrO-P\textsubscript{2}O\textsubscript{5}-SiO\textsubscript{2}/BaO-P\textsubscript{2}O\textsubscript{5}-SiO\textsubscript{2} and SrO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}/BaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} ternaries result from the TOC for BaO being positive, whereas the TOC for SrO is negative.\textsuperscript{3}

### 4.4 | Intrinsically low Brillouin scattering glasses

In a similar manner, the deduced transverse $p_{12}$ photoelasticity values are shown in Figure 9 for the same glass families. The counterplay between positive and negative $p_{12}$ compounds that was discussed in Companion Papers I and II,\textsuperscript{1,3} can most clearly be seen in the ternaries comprising Al\textsubscript{2}O\textsubscript{3}, SrO, and BaO. As expected, given the weak and only slightly negative $p_{12}$ value for Al\textsubscript{2}O\textsubscript{3}, the zero $p_{12}$ compositions necessarily occur at Al\textsubscript{2}O\textsubscript{3} concentrations too high to likely be feasibly made into glass and drawn into fibers.

However, both SrO and BaO possess sufficiently large and negative $p_{12}$ values that it is reasonable to expect that bulk glasses could be formed at $p_{12} = 0$ ternary compositions where Brillouin scattering should be negated.
Although mapping out individual material parameters, for example, $p$, TOC, and $p_{12}$, that most influence a given nonlinearity is useful, it is more impactful to understand, where able, all of the underlying factors taken together. Such a complete property value ternary representation is shown in Figure 10 for the Brillouin gain coefficient, BGC, associated with the same systems as described above. Each of the factors used to compute the BGC, as described in Companion Paper I, were deduced using the approaches described in Companion Papers II.2,3

Given the dependence of the BGC on multiple properties ($n$, $p_{12}$, $\nu$, $V_a$, $\Delta V_B$), each one possessing its own compositional trends, the curvature of the contour lines are more complicated than in the single property ternary diagrams; for example, Figures 7-9. In the ternary diagrams, this manifests interesting and occasionally unexpected compositional trends.

The individual BGC binaries that comprise the GeO$_2$-, P$_2$O$_5$-, B$_2$O$_3$-related ternaries with SiO$_2$ were shown in Figure 6 of Companion Paper IIB and, not surprisingly, those trends are equally evident in Figure 10. In short, while some reductions (3-8 dB) in BGC result from doping SiO$_2$ with these conventional telecommunication dopants, they do not offer marked mitigations. Important (>10 dB) reductions are possible with $p_{12} < 0$ dopants, such as Al$_2$O$_3$, SrO, and BaO. As noted with respect to Figure 9, it is the large and negative $p_{12}$ values of the alkaline earth oxides that lead to significant (>15 dB) reductions in BGC even at reasonably high SiO$_2$ concentrations of about 80 mol%.

The representations of Figure 10 can be overlaid with similarly important reductions in other parameters, such as in the TOC that drives transverse mode instability (TMI). As a case in point, Figure 11 provides a comparison of compositions that provide significant reductions in both SBS (>15 dB) and TMI (>5 dB), relative to conventional single-mode fiber, based on the BGC and TOC property value diagrams of Figures 10 and 8.

5 | MODELING OF THE HIGH-POWER/-ENERGY PERFORMANCE

The power scaling potential of the intrinsically low nonlinearity fibers fabricated to date were modeled using the procedures described in Ref. 52. These results, compared to values for conventional Yb$^{3+}$-doped silica fiber lasers, are presented in Figure 12 with the underlying known and
estimated material parameters provided in Table 2. As in Ref. 52, the simplest fiber geometry is assumed (no advanced waveguide schemes) and for the SBS-limited case, single frequency amplification is assumed. Controlled line broadening is well known to increase the SBS-limited output power, however, when this technique is employed, one must understand the acceptable line-broadening allowed by the application as well as the SBS linewidth of the proposed material. The SBS linewidth is not included in Table 2 and is not relevant to Figure 12 due to the assumption of single frequency amplification for the SBS-limited case.

It is important to note that the research by Dawson et al., pre-dates the discovery of transverse modal instability, TMI. Given that a simple predictive model for transverse modal instability is still not fully formed and agreed upon, included here is the better understood effect of thermal lensing as an (imperfect) proxy for transverse modal instability. A study of Table 2 will reveal that a number of important material properties are not known for the candidate all-glass fibers treated: YAG-derived yttrium aluminosilicates, sapphire-derived aluminosilicates, and low-silica content strontium aluminosilicates. Of these, damage threshold and thermal conductivity are the greatest sources of uncertainty in the calculation that produced Figure 12.

The graphs in Figure 12 are generated by the methodology of Dawson et al. In this methodology, the physical effects that limit the power scaling of a single-fiber laser are expressed as functions of fiber core diameter and fiber length. All parameters except core diameter and fiber length are either state-of-the-art parameters (such as diode

### Table 2: Material parameters employed for the calculation of power scaling plots based on Ref. 52

| Property (unit) | Conventional value for SiO₂ | YAG-derived yttrium aluminosilicates | Sapphire-derived aluminosilicates | Low-silica strontium aluminosilicates |
|----------------|----------------------------|--------------------------------------|-----------------------------------|--------------------------------------|
| Non-SiO₂ Content (mole %) | – | Al₂O₃: 19.9 | Al₂O₃: 54.0 | SrO: 23.7 |
| Rupture Modulus Rₘ (W/m) | 4300 | 4300 | 4300 | 4300 |
| Thermal Conductivity κ (W/mK) | 1.38 | 1.38 | 1.38 | 1.38 |
| Convective film coefficient h (W/m²K) | 10000 | 10000 | 10000 | 10000 |
| Melt temperature Tₘ(K) | 1983 | 1983 | 1983 | 1983 |
| dn/dT (K⁻¹) | 1.18 × 10⁻⁶ | 1.01 × 10⁻⁶ | 1.19 × 10⁻⁶ | 5.3 × 10⁻⁶ |
| gₚ (m/W) | 1 × 10⁻¹³ | 0.52 × 10⁻¹³ | 0.54 × 10⁻¹³ | 0.5 × 10⁻¹³ (est.) |
| BGC (m/W) | 5 × 10⁻¹¹ | 0.5 × 10⁻¹¹ | 3.1 × 10⁻¹³ | 2.2 × 10⁻¹³ |
| A | 20 | 20 | 20 | 20 |
| G | 10 | 10 | 10 | 10 |
| Γ | 0.8 | 0.8 | 0.8 | 0.8 |
| Damage threshold Iₜₜₜ (W/μm²) | 35 | 35 | 35 | 35 |
| Tₑ (K) | 300 | 300 | 300 | 300 |
| Iₚₒₒₑ (W/μm²/sr) | 0.1 | 0.1 | 0.1 | 0.1 |
| αcore (dB/m) | 250 | 1500 | 1500 | 1500 |
| ηlaser | 0.85 | 0.85 | 0.85 | 0.85 |
| ηheat | 0.1 | 0.1 | 0.1 | 0.1 |
| NA | 0.45 | 0.45 | 0.45 | 0.45 |
| λ (nm) | 1088 | 1088 | 1088 | 1088 |

*Where not specified, see Ref. 52 for details on a given property.

*Values are unknown for the 3 aluminosilicate systems but, given their relatively high SiO₂ contents, the values for silica are employed as a limit.

*Values reasonably carried over to the 3 aluminosilicate systems.

*Tailorable via precursor Yb concentration.
FIGURE 7 Contribution of density fluctuations to Rayleigh scattering: ternary diagrams of hydrostatic photoelasticity coefficient, \( p = p_{12} + (2/3)p_{44} \), for selected compositional families. Values are deduced using the approaches described in Companion Papers II,III [Color figure can be viewed at wileyonlinelibrary.com]
FIGURE 8 Stimulated thermal Rayleigh scattering (STRS): ternary diagrams of thermo-optic coefficient, TOC \((dn/dT)\), for selected compositional families. Values are deduced using the approaches described in Companion Papers II\(^2\),\(^3\) [Color figure can be viewed at wileyonlinelibrary.com]
FIGURE 9  Brillouin scattering: ternary diagrams of transverse photoelasticity coefficient, $p_{12}$, for selected compositional families. Values are deduced using the approaches described in Companion Papers II. [Color figure can be viewed at wileyonlinelibrary.com]
FIGURE 10  Stimulated Brillouin scattering (SBS): ternary diagrams of the Brillouin gain coefficient, BGC, for selected compositional families. Values are deduced using the approaches described in Companion Papers II²,³ [Color figure can be viewed at wileyonlinelibrary.com]
laser brightness, which is generally improving with time) or physical constants of the material system, which are varied to greater extent in this trilogy. The main physical effects that are considered are thermal (melting, rupture, lensing), optical nonlinearities (SRS and SBS, note these are typically considered on separate plots depending upon which one dominates based on laser spectral line-width), optical damage and limitations on pump power. Pump power limitations come about from the necessity for a high-power laser to be efficient in order to be practical. This requirement means that most of the pump light must be absorbed in the length of the fiber. Thus, Dawson et al\textsuperscript{52} show that if the fiber length is known, then the core diameter, doping concentration, and state-of-the-art diode brightness determine the allowed fiber cladding diameter, which in turn limits the total coupled pump power. As the fiber laser efficiency is typically ~85\%, this, in turn, creates a power-limit based on the amount of pump power that can be efficiently coupled into the fiber laser.

The contour plots in Figure 12 are formed by calculating all the physical limits for each pair of coordinates (core diameter and fiber length) and plotting the lowest limit. What emerges are regions where different limits dominate. At the smallest core diameters and shortest lengths (lower left hand corner of the graphs), the pump-coupling limit typically dominates. For large core diameters and short fiber lengths (lower right side of the plots), the heat load per unit length is high and thermal effects typically are dominant. For small core diameters and long lengths (upper left side of the plots), the light is intense over a long length of fiber and either damage or nonlinear optical effects limit the fiber output power. A key finding of Dawson et al\textsuperscript{52} is that the interaction of thermal and

**FIGURE 11** Representative ternary compositional diagrams overlaying both Brillouin gain coefficient, BGC, and thermo-optic coefficient, TOC, relative to those for conventional telecommunications single mode fiber, for the reduced magnitudes for these nonlinearities that are the goal of this Trilogy [Color figure can be viewed at wileyonlinelibrary.com]
FIGURE 12  Power scaling diagrams representing the threshold optical power levels where power scaling is limited by either pump brightness, laser damage, thermal lensing, and (A) stimulated Raman scattering (SRS) and (B) stimulated Brillouin scattering (SBS) regimes. In both sets of Figures, the optical fibers modeled are: (i) conventional SiO$_2$, (ii) YAG derived yttrium aluminosilicate glass, (iii) sapphire derived aluminosilicate glass, (iv) strontium aluminosilicate glass. Property values that yielded these modeled results are provided in Table 2. The maximum achievable power is noted in the box [Color figure can be viewed at wileyonlinelibrary.com]
nonlinear effects typically set a hard upper limit on output power from a single optical fiber laser for a given material system that is largely independent of core diameter and fiber length, although there is a specific length associated with each core diameter at which this limit is attained. Below, the variations of material parameters considered in this paper are discussed in terms of how they affect the relative size of the regions and ultimate scaling limit of a given material system.

Four main parameters are assumed to be improved in the three materials: rare-earth doping concentration, TOC (dn/dT), Raman, and Brillouin gain coefficients. The primary impact of increased doping concentration is to reduce the parameter space over which limited pump-coupling dominates the fiber laser output power. More specifically:

- **YAG-derived yttrium aluminosilicates**: A slight increase in the SRS-limited power due to reduced Raman gain coefficient is observed as is an expected reduction in pump-limited parameter space. However, this reduction is offset by the formation of a damage threshold-limited region (again, accurate knowledge of the damage threshold is needed). The SBS-limited case shows a > three-fold increase in output power due to a significant reduction in the BGC. Importantly, this is attained at a 40 μm core diameter due to the reduction in the pump-limited parameter space.

- **Sapphire-derived aluminosilicates**: As with the YAG-derived glass, slight improvements are observed in the SRS-limited case other than the reduction in the pump-limited zone and appearance of the damage-limited zone. However, there is now a dramatic increase in the SBS-limited power to >10 times the conventional silica case. This is a direct result of the 100 times decrease in BGC. Core size remains in the 40 μm region, a relatively practical zone from the standpoint of both fabrication and bending.

- **Low-silica strontium aluminosilicates**: In this case a 2 time increase in power in the SRS-limited power is observed due to the reduced Raman gain and reduced TOC. Here, the calculation’s exclusion of an analysis of TMI is cause for some skepticism of this result. The SBS-limited case shows a further increase in the SBS-limited power due to the additional reduction in the SBS gain coefficient as well as the reduction in TOC.

Overall, these results show promise for improved materials for high-energy lasers, particularly narrow bandwidth lasers limited by SBS. The improvements are predominantly due to the increase in doping concentration (reduction in SiO2 content), which allows the maximum power to be attained at smaller core diameters which reduces thermal effects in general, and is known to be desirable for decreased TMI as the purely single-mode waveguide regime is more effectively maintained. Furthermore, dramatically reduced Brillouin gain greatly raises the power threshold for the onset of SBS. Note the maximum power in the SBS case increases as the square root of the reciprocal of the BGC per Equation 27 in Ref. 52. This suggests further development of these classes of materials are a promising approach for scaling power in SBS-limited fiber laser systems with the caveat that a number of the assumed material parameters in Table 2 need to be determined and Figure 12 needs to be updated to validate that the true values of these parameters do not affect the conclusions made here.

## 6 Toward the “Perfect” Optical Fiber

With respect to the best results to date, “best,” is somewhat arbitrary as the ideal case is one where all of the nonlinearities are reduced by levels that make the fiber more practical. For example, while ~20 dB suppression has been achieved in a sapphire-derived, high-alumina-content aluminosilicate glass fibers, these fibers were highly multimoded and exhibited a 2.5 dB suppression in Raman gain. In terms of collective reductions in nonlinearities, as is the focus of this Trilogy, an oxyfluoride fiber might represent a “better” opportunity in that initial efforts already have shown nearly single mode operation with worthy reductions in gR (~0.9 dB), dn/dT (~2.2 dB), and BGC (~6.3 dB), relative to conventional optical fiber.55

This section stakes a flag in the ground for the “perfect” fiber. As noted in Table 1 of Companion Paper I, and described in terms of specific compositions in this paper, each of the parasitic nonlinearities possess the potential to be wholly negated. In some cases, such as with Raman scattering and n2-related wave-mixing, the necessary conditions of Λ = 0 and n2 = 0, respectively, although theoretically possible, seem at present not materially practical. However, the two main phenomena that presently limit power scaling in high-power fiber laser systems, namely SBS and TMI, should be quite reasonably mitigated. In these cases, the p12 = 0 and dn/dT = 0 conditions, respectively, are well-defined over large, yet practical, compositional ranges. Of particular interest are compositional spaces where these zero points approximately coincide. Examples of these are those shown in Figure 13, which, along with the aforementioned p12 = 0 and dn/dT = 0 compositions, includes p = 0 compositions where the density-related contribution to Rayleigh scattering also would be zero.
Admittedly (and purposefully) provocative, the compositions identified herein that exhibit markedly reduced collective nonlinearities are beyond the capabilities of industry standard CVD processes used to fabricate conventional (telecom) optical fibers. High-silica-content CVD-derived fibers will remain the industry standard for long-haul communications with evolutionary progress in attenuation being made through process-related thermal history (fictive temperature) and minor dopant engineering. However, to be clear, in order to achieve the power scaling goals of high-power/-energy, high beam quality fiber-based lasers, conventional CVD processes will not be sufficient due to the limited compositional ranges such processes mandate as noted in the Section 1. Structural/geometric approaches, such as those associated with microstructured and photonic crystal fibers, employing conventional CVD-derived high silica content glasses, certainly will continue to make incremental improvements. But, revolutionary advances such as >20-30 dB reductions, or even the wholesale negation of Brillouin-related SBS and thermo-optic-related STRS-induced TMI, can only be achieved through a unified materials approach, whereby parasitic nonlinearities are addressed at their fundamental origins. This will necessitate the fiber laser community to adopt a new mindset as relates to the centrality of glass science and engineering.

To date, the molten core method appears to be the best approach to achieve optical fibers possessing the intrinsically low nonlinearity compositions identified in this Trilogy. This is due in large part to the fact that many of the compositions are inherently prone to phase separation. As such, bulk glass melting followed by rod/tube fabrication and conventional drawing may not yield high quality, low loss fiber.

While the molten core approach has proven its compositional flexibility, future efforts need to focus on reducing attenuation. Although there is nothing intrinsic about the process that should lead to enhanced optical losses, three factors seem to contribute most significantly to the measured attenuation values. First, the purity of the precursor phase is paramount. The lowest loss molten core-derived fibers to date have been those fabricated using commercial single crystals; specifically the yttrium aluminosilicate glass optical fibers derived from single crystalline yttrium aluminum garnet (YAG), which exhibited losses on the order of 100 dB/km. Second, the presence of OH species in the glass also can lead to parasitic losses. In the molten core-derived fibers, the OH content also depends on the nature of the core precursors employed. When commercially grown bulk crystals are employed, the OH contents can be quite low. The (single crystal) sapphire-derived aluminosilicate fibers described originally in Ref. 51, exhibited virtually no measured additional OH-related losses. Fibers derived from commercial powders, such as the BaO-derived bariosilicate of Ref. 58 exhibited higher OH-related losses; ~8dB/m at a characteristic wavelength of 1390 nm. Third, extrinsic losses may also arise from scattering due to nanoscale phase separation associated with some of the compositions detailed herein traversing liquid-liquid
immiscibility regions on cooling from above the upper consolute point to their glassy state as the (molten core) fiber draws. Such immiscibilities can be lessened by the addition of alumina,\textsuperscript{89} for example, which would also further reduce the BGC and \( g_R \) of the resultant glass.

Interestingly, and importantly, the \(-100 \text{ dB/km}\) value achieved to date is only a factor of only 2-5 times higher than the 20-50 dB/km level considered practical for laser and amplifier fibers since use-lengths are on the order 10-15 meters. Indeed, as noted above, sub-20-30 dB/km loss values have been obtained from powder-derived fibers\textsuperscript{8,60} so achieving optical fibers with practical losses from such highly modified silicate compositions is not unreasonable.

7 | CONCLUSIONS

This paper provides a road map to glass compositions that would markedly reduce the optical nonlinearities that plague the scaling to higher output powers in present telecommunication and high-power fiber lasers. More specifically, based on the theoretical foundations of Companion Paper I,\textsuperscript{1} coupled with the property additivity relations of Companion Papers II,\textsuperscript{2,3} described here are compositional trends to tailor Brillouin-, Raman-, Rayleigh-, thermo-optic-, and \( \chi^{(3)} \)-related material properties. Examples from existing fibers and bulk glasses are generated where data are available. Furthermore, ternary property value diagrams are generated to more easily represent and identify compositional regions where the greatest opportunities for mitigating nonlinearities are possible. In the specific case of yttrium and strontium aluminosilicate fibers, variations in the material could lead to power increases of \( 2-3 \times \) or more over current fiber lasers based on classical fused silica compositions. Note this is before other effects such as deliberate line width broadening or advanced waveguide design are employed to further scale the output power. Furthermore, the impact of higher concentration by itself should not be underestimated as it simplifies the overall requirements on the diode laser portion of the integrated system. Oxyfluoride aluminosilicate glasses containing alkaline earth compounds, potentially with \( \text{B}_2\text{O}_3 \) and \( \text{P}_2\text{O}_5 \) additions, are especially worthy of further consideration based on their potential to significantly reduce Brillouin, Raman, Rayleigh, and stimulated thermal Rayleigh scattering while possessing a nonlinear refractive index comparable to conventional silica and could potentially lead to much greater power scaling if, for example, the BGC could be reduced beyond that assumed in Table 2.

Secondary intentions of this work are to reassert the power of glass science in the performance of modern optical fibers and to evoke a reconsideration of the processing methods employed for the fabrication of specialty optical fibers (eg, molten core). As shown in this Trilogy, the ability of glasses that are based on common compounds to exhibit such remarkable performance, such as the potential to negate optical nonlinearities, which is impossible even in the most complex and sophisticated microstructured and photonic crystal fiber designs, certainly supports the goal of these intentions.

Lastly, and with purposeful provocation, is the hope that this Trilogy serves as a clarion call for the development and acceptance of new material and fabrication approaches to be considered and evaluated. This is actually born out of the realization that conventional CVD processes are incompatible with the compositions identified herein as enabling truly revolutionary material-driven advances in optical power scaling in fiber laser systems. The primary focus on high-energy fiber lasers makes such a prospect not unreasonable given that relatively short fiber lengths (tens of meters) are employed and higher losses (~20 dB/km) than required for long-haul communications are acceptable. With apologies to Oren Harari, the readers of this Trilogy, along with members of the broader glass, fiber, and laser communities are reminded that the laser did not arise from continuous improvements to the light bulb.

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