Non-Linear Optical Materials: Advancements Exemplified by Fluorooxoborates

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Non-linear optics (NLO) represent a complex yet essential part of scientific infrastructure. Under normal circumstances, the linear part of a material's optical response will dominate, and so well-understood phenomena like frequency conservation and superposition are observed. However, at very high intensities such as those seen in pulsed laser systems, the second or higher order (non-linear) polarization terms will become prominent. At their core, NLO materials are materials that exhibit some such non-linear response to light, such as optical parametric generation, the optical Kerr effect, or high harmonic generation[1]. The intelligent design of such materials has facilitated great advancements across the scientific disciplines. For example, NLO crystals such as β-BaB$_2$O$_4$ (BBO) allow laser systems to probe significantly broader spectral regions, significantly enhancing the experimental capabilities of physical chemistry laboratories. Fluorooxoborates are an emerging class of crystals that expand NLO properties into the ultraviolet (UV) and deep-UV (DUV) regions[2]. In this literature seminar, the development of fluorooxoborates is used to exemplify the design goals and challenges of NLO materials.

Fluorooxoborates consist of metal cations binding with various boron-oxygen-flourine anions[2] (**Figure 1**). To understand the design considerations for fluorooxoborates, one must first understand their potential application. Fluorooxoborates have been proposed as solid-state substitutes for excimer lasers. Current excimer lasers rely on a combination of noble and halogen gases to produce laser pulses in the UV region, and this approach comes with the disadvantages of bulky equipment, inconsistent beam performance, and toxicity – problems a fluorooxoborate all-solid-state-laser could avoid[3]. Fluoro-oxoborates generate UV laser pulses using second-harmonic generation (SHG), a NLO wherein two photons interact to form a new photon with double the original frequency. Fluorooxoborates must thus satisfy the following requirements: they must have strong SHG response; they must have a large transparent window into the UV; they must have significant birefringence to allow for proper phase-matching; and they must allow for stable, easy growth of large single crystals[4].

The first requirement of a NLO material is that it displays NLO processes. In order for fluorooxoborates to be viable, they must therefore demonstrate appreciable SHG. The physical description of SHG can be directly calculated from Maxwell's equations, but the derivation is trivial and so left to the reader[1,5].
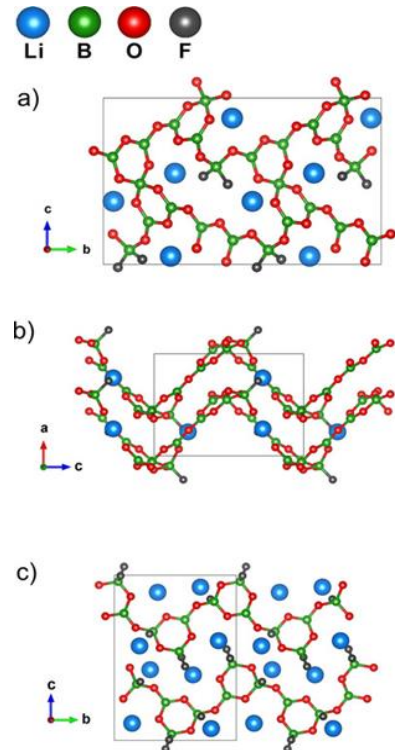

Figure 1: Example fluorooxoborates[2]. a) Li$_2$B$_6$O$_9$F$_2$, b) LiB$_6$O$_9$F, and c) Li$_2$B$_3$O$_4$F$_3$.
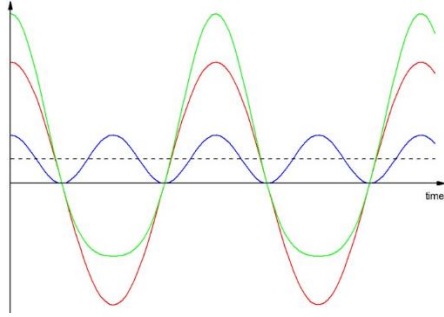
Figure 2: Response (green line) of a medium to a driving field (red line) as the result of OR (dashed black line) and SHG (blue line) [5]

Ultimately, the second-order non-linear polarization breaks into two terms[5] dependent on the electric field, one constant and one oscillating: $P^{(2)}(t) = \varepsilon_0 \chi^{(2)} EE = \frac{1}{2}\varepsilon_0 \chi^{(2)} \widehat{E}\,\widehat{E}^* + \frac{1}{4}\varepsilon_0 \chi^{(2)} \widehat{E}^2 e^{i2\omega t} + \text{c.c.}$ The constant term represents optical rectification, and the oscillating term represents SHG. Intuitively, the constant term represents a shift in the net positions of the ions in the crystal lattice, and thus the responding electric field will be shifted upwards compared to the driving field. In order for this to occur, an oscillating electric field with double the frequency of the driving field must be produced, and this is SHG (**Figure 2**). The equation informs the search for SHG materials. Since SHG results from a second order (and therefore even) process, only non-centrosymmetric materials may undergo SHG. As centrosymmetric materials have inversion-symmetric electric susceptibilities, they would produce equal positive and negative polarizations, which can only be true if the polarization is zero[6]. Further, larger $\chi^{(2)}$ coefficients will yield stronger SHG. Chen et al. attempted to elucidate this trend with anionic group theory, which states that the anionic groups dominate the NLO process[7]. Both computationally and experimentally, borates have well-defined large $\chi^{(2)}$ coefficients and so are ideal for SHG crystals[8,9]. Fluorinated borates have been shown to have similar properties (**Figure 3**)[10]. Cations, however, do still play a role in arranging and orienting the borate anions[11]. Consequently, the development of fluorooxoborates may be seen as finding the optimal combination of fluorination with choice of metal cation.

Simply having SHG does not automatically mean the process will produce a usable beam. The SHG process occurs throughout the entirety of the driving beam's path through the crystal. Because second harmonic photons have a different frequency than the driving photons, they will have different effective indexes of refraction, and so they will travel through the material with different velocities. This means that the second harmonic photons generated later can be in different phases than the earlier ones. If not accounted for, phase mismatch results in destructive interference that drastically decreases the resulting intensity[1,12]. To compensate for this, NLO materials must employ some form of phase-matching[12,18]. For single crystals such as fluorooxoborates, this phase-matching is achieved by exploiting the birefringence of the material. Birefringence is the property of anisotropic crystals wherein the refractive index changes based on the polarization and propagation direction of the transmitted light. By modifying the crystal's temperature (non-critical phase matching) or the incident beam's propagation angle (critical phase matching), the two frequencies can be made to have the same effective refractive index, and thus remain in phase[12]. In fluorooxoborates, the flatness of the boron-oxygen-fluorine layers increases optical anisotropy between the axes parallel and orthogonal to the plane[2]. This is enhanced by the BO_3F anion's large polarizability difference parallel versus perpendicular to the B-F bond[13] (**Figure 3**). However, the flatness also means that larger deviation angles are required for phase matching. Still, by tuning the cation, fluorooxoborates can be made with sufficient birefringence for proper phase-matching.

In order to generate or transmit UV or DUV light, the material obviously must not absorb in those regions. Absorption in this range can stem from two sources. First, there are the electronic
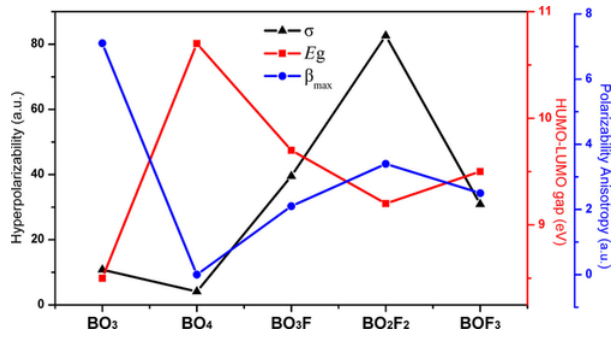
Figure 3: Calculated properties of fluorooxoborate anionic groups[2]

transitions of the metal cations. Metals with d-d or f-f transitions can absorb in this region, and so elemental selection is limited to alkali and alkaline earth metals. Second, there is the absorption of the various borate anionic units[8]. DFT calculations show that the addition of fluorine raises the HOMO-LUMO band gap energy of the borate anion[14] (**Figure 3**), leading to a band gap energy range between ~8.5 to 11 eV (146 to 113 nm). In certain systems, the oxygens of the borates would have unsatisfied octets; this creates a so-called "dangling bond" which significantly decreases the band gap. In these crystalline systems, however, the dangling bonds are interlinked with the metal cations, eliminating their damaging effects[11,15]. Taken as a whole, these properties mean fluorooxoborates are transparent in the required regime.

Despite the stringency of the above considerations, two seemingly viable crystals – $KBe_2BO_3F_2$ (KBBF) and $RbBe_2BO_3F$ (RBBF) – have existed for decades prior to the discovery of fluorooxoborates[8]. These crystals, however, failed to find widespread use due to their impracticality. KBBF and RBBF require toxic BeO to synthesize, and, further, tend to layer along their optical axis, which makes single-crystal growth exceedingly difficult. In order to be viable for use in laser systems, fluorooxoborates must also be practical. Unfortunately, unlike the SHG response or the birefringence, these practical considerations are difficult to predict without directly making the crystal. Still, chemical intuition and creative tinkering can help guide development. Jansen et al. – the group who first synthesized a fluorooxoborate – developed the basic synthetic steps: boron oxide or an alkali oxoborate functions as a Lewis acid that reacts with the Lewis base alkali fluorides or tetrafluoroborates[16]. Due to the volatility of fluorine, the reactions must be run in sealed containers. Further, because BF_3 is sensitive to water, all components must be dried extensively. The largest single crystals obtained come from a modified hydrothermal synthesis[17]. Instead of using water, boric acid or ethylamine-borontrifluoride is used as the flux in the autoclave, preventing unwanted reactions. While not unique to NLO, these practical synthetic considerations play a significant role in NLO development nevertheless.

The development of fluorooxoborates exemplifies the development of modern NLO materials. First, the non-linear processes (second-harmonic generation, phase matching) must be prominent. Second, the ordinary optical processes (transmittance window) must be viable. Lastly, the normal practical considerations (synthesis, safety) must allow for actual use. When all these design challenges are overcome, the material can support advancement across many scientific fields.

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