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Strategy and Tactics in the Search for New
Harmonic Generating Crystals *

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Abstract

Three basic questions must be answered to ensure success in the search for an optimized nonlinear crystal for a particular application: What are the most important optical properties which determine the crystal's figure of merit for the intended application? What is the best methodology for characterizing those optical properties so that materials of interest can be identified efficiently? Where in "materials space" can crystals with such properties be found with the highest probability? Answers to these questions will be discussed in the context of a program to find improved frequency conversion crystals for high power lasers.

Introduction

It is generally recognized that practical high efficiency harmonic generation of very low power lasers (such as laser diodes) requires crystals with large nonlinear coefficients. This has spurred the search for such materials in many laboratories. It is less often appreciated that efficient conversion of very high power lasers is also materials limited. Even multimewatt pulsed lasers are rarely frequency converted with more than about 60% efficiency in general practice, even though simple theoretical calculations might imply that much greater efficiency should be possible at those power levels.

Harmonic conversion efficiencies far less than unity are often, of necessity, accepted in laser design. However, in many cases this represents a severe blow to the overall ("wallplug") efficiency of a laser system, ultimately increasing the size and cost of a unit which must supply a certain desired amount of light at the harmonically generated wavelength. One area where the economic impact of frequency conversion efficiency is very clearly felt is in high power solid state laser systems used for inertial confinement fusion (ICF).⁽²⁾ Here, it is currently believed that blue or near ultraviolet light is optimum for efficient compression of the fusion target, but the large aperture Nd:glass lasers used in these experiments produce near infrared light with a wavelength of 1.05 μm . To generate shorter wavelength light, nonlinear crystals are used to frequency double to 0.527 μm , and this doubled light is then mixed with the residual fundamental to produce light at 0.351 μm . This latter frequency mixing process is colloquially known as third harmonic generation (THG) or "tripling". KDP, whose optical properties and threshold powers have recently been reviewed,⁽²⁾ is the material currently used for this purpose. On the NOVA fusion laser operated at Lawrence Livermore National Laboratory, for example, 70% conversion to the ultraviolet has been observed using KDP.^(3,4) Thus, nearly 1/3 of the light energy generated by this 100KJ laser system remains in the form of longer wavelength photons less useful for target compression.

Less than unity conversion of high power lasers is an unavoidable consequence of laser beam divergence.^(5,6) Eimerl has suggested recently on intuitive grounds that the performance limit for a given nonlinear crystal for a particular harmonic generating process is determined by a figure of merit called the "threshold power," which is a function of both the nonlinearity d_{eff} and angular sensitivity β of the crystal ^(5,6):

$$P_{\text{th}} \propto (\beta/d_{\text{eff}})^2$$

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The lower the threshold power, the easier it is to achieve high conversion efficiency of the noisy pulses and aberrated beams which are typical of high-power lasers. Materials with threshold powers an order of magnitude lower than KDP could achieve conversion efficiencies closer to 90% for beam of similar quality to Nova. This has motivated us to undertake a broad and systematic search for such crystals.

The frequency conversion materials which are useful in Nd:glass based fusion lasers of recent design must satisfy several other criteria besides having a low threshold power. First, they must be transparent to wavelengths as short as $0.264\text{ }\mu\text{m}$ to preclude substantial two photon absorption of the intermediate $0.527\text{ }\mu\text{m}$ light, which can cause loss of THG efficiency and possibly photochemical damage to the crystals. (Strictly speaking, two photon absorption of the $0.351\text{ }\mu\text{m}$ light is also unwanted, but its effect on conversion efficiency is less deleterious.) Second, because the next generation of fusion lasers is designed to operate at (infrared) fluences as high as 40 J/cm^2 , the frequency conversion crystals ideally should operate at these fluences without optical damage. Current laser designs also specify single segment apertures of $25 - 30\text{ cm}$ on a side.^(4,7) While such large aperture frequency convertors could be constructed from many smaller sized crystals, this severely compromises the beam quality of the generated harmonic light, and could lead to unacceptable optical losses. Therefore, crystals for ICF lasers must be growable to sizes which allow $30 \times 30\text{ cm}^2$ plates to be fabricated. While there is no fundamental reason why high temperature flux or melt grown crystals could not be used for this application, substantial experience with crystal growth indicates that water soluble crystals are most likely to meet the growth and damage threshold requirements. In fact, KDP is the only frequency conversion material currently available in high quality pieces this size.

The transparency requirement quoted above immediately sets a limit on the maximum size of the nonlinearity we can expect to find in such materials. Data for known nonlinear crystals implies that it is unlikely to find crystals with phase-matchable d coefficients much greater than 2 pm/V if their UV edge is shorter than 250 nm . Although the size of the d coefficients is bounded by the transparency requirement, threshold powers substantially smaller than those of KDP can still be achieved by finding crystals which have much smaller angular sensitivities than KDP. This requires that either the crystals have low birefringences or that they have noncritical, or near noncritical phasematching orientations. This depends, in turn, on a fortuitous equality of birefringence and dispersion.

The probability of finding a new nonlinear crystal with such specific optical characteristics within a reasonable period of time depends on several factors. The first factor is the rate at which the relevant optical properties can be measured with sufficient accuracy to decide if the crystal is likely to be better than the ones already in hand. Second, there must be a reasonably high probability that the set of materials chosen for characterization contains crystals with the desired characteristics. Finally, assuming that crystals with the desired properties are only sparsely distributed among the set, the rate at which the crystals can be synthesized or otherwise obtained in characterizable form must be high, so that a large population of crystals can be scrutinized. The object of this paper is to review the strategy we have developed to optimize these factors in our search for improved ICF frequency convertors.

The next section briefly describes an efficient screening procedure which we have developed for identifying potential frequency convertors for fusion lasers. Section III discusses the chiral organic salt strategy which we have used to generate a large population of phasematchable crystals with many of the desired characteristics for ICF. Section IV presents a statistical model we used to estimate the probability of finding low threshold power harmonic generators in this class of materials. The specific phasematching properties of some new nonlinear crystals from this class are discussed in section V. Section VI contains some concluding remarks.

It is important to note that, with the exception of the extraordinarily large aperture size requirement, the criteria for a fusion laser frequency convertor are generally applicable to any high power laser. Moreover, many of the ideas presented here are applicable, mutatis mutandis, to the search for NLO crystals for any specific application, for example, diode laser doubling.

Efficient Screening of Harmonic Generating Crystals

The basic objective of our screening method is to identify those materials which are likely to be less angularly sensitive and more nonlinear than KDP for frequency doubling or tripling 1.05 μm light without the need to grow large, high quality crystals. In principle, it is possible to evaluate these properties by powder SHG experiments alone. (8-9) In practice, however, we have found that powder SHG tests for phasematching and for determining noncritical wavelengths are too often ambiguous to be useful in a large survey. Therefore, we have used powder SHG tests only as a means of identifying crystals with nonlinear coefficients as large or larger than those of KDP. A description of our powder apparatus and experimental method has been given elsewhere. (10-11) An important observation we have made is that, depending on particle morphology, a material with nonlinear coefficients the same size as those of KDP can easily exhibit a powder SHG signal as low as 1/2 or as high as 2x that of KDP itself. In this sense, the "uncertainty" of the powder measurement made on a new material is a factor of 2, and we accept for further characterization those materials which have a powder signal 1/2 of KDP or greater. While this sends some crystals with nonlinearities smaller than KDP to the next level of characterization, it ensures that we do not reject too many crystals which do have the desired nonlinearity.

The next step is to identify those crystals which also have low angular sensitivities for phasematched doubling or tripling. The most accurate method of determining such properties is to measure the wavelength dependence of the refractive indices and calculate the phasematching orientations and angular sensitivities using the exact phasematching equations which have been given by a number of authors. (12-13) Since the vast majority of crystals we study are biaxial, this would take too much time and effort to be useful for a rapid survey. Instead, we have developed an approximate method for determining phasematching properties which is rapid and complements the powder SHG screening step. The method relies on a determination of the refractive indices at a single visible wavelength or, more typically in practice, for white light. (11,14)

At a single wavelength, the refractive index ellipsoid of a biaxial crystal is specified by three principal refractive indices $n_\alpha < n_\beta < n_\gamma$ from which are derived the principal birefringence $\Delta = n_\gamma - n_\alpha$, and the optic angle V as defined in Figure 1. For phasematching processes which lie well within the transparency range of the crystal, there exists a simple approximate formula for the locus of phasematching orientations (θ, ϕ) :

$$\begin{aligned} \sin^4 \theta \sin^2(\phi + V) \sin^2(\phi - V) + \cos^2 \theta \sin^2 \theta (\sin^2(\phi + V) + \sin^2(\phi - V)) \\ + \cos^4 \theta = (\delta/\Delta)^2 \end{aligned}$$

which depends on the principle birefringence Δ , and the optic angle V evaluated at the fundamental wavelength, and the difference between the average refractive indices at the fundamental and harmonic wavelengths, $\delta = n(2\omega) - n(\omega)$. We refer to the parameter δ as the "dispersion" of the crystal's refractive indices.

For nearly all the crystals we have studied, the principal birefringence and the optic angle vary only slightly with wavelength. Therefore, the white light indices give reasonably accurate

values of these parameters over the entire transparency range of the crystals. The dispersion parameter δ can be estimated from the magnitudes of the refractive indices themselves, using a crude empirical model.(11,14) From the estimated dispersion, the principal birefringence, and the optic axial angle we can generate representations of the phasematching loci for SHG and THG which usually lie within $\pm 10^\circ$ of the true loci. This information is sufficient to indicate if angularly insensitive orientations exist. Examples of these approximate loci are shown in Figure 2, along with the exact (experimentally measured) loci for comparison.

If this approximate method predicts that the crystal has phasematching orientations which are angularly insensitive, then more complete and accurate determinations of the refractive indices as a function of wavelength are made using a unique microrefractometer developed in our laboratory.(15-16) Single crystallites as small as 50 μm are easily characterized using this technique, although currently it is limited to crystals which have refractive indices smaller than 1.7. The refractive indices determined this way are usually accurate to $\pm 2 \times 10^{-4}$, although larger errors are sometimes observed in the ultraviolet. For doubling 1.05 μm , the phasematching angles calculated using the refractive indices determined from microrefractometry are typically within 2° of those determined by direct phasematching measurements or by calculations using prism data. For sum frequency generation to produce 0.351 μm , the calculated phasematching angles are accurate to $\pm 5^\circ$.

At this stage, we have screened out a set of materials which are very likely to be more nonlinear than KDP and are very certain to have phasematching orientations which are less angularly sensitive. However, for a crystal to have a low threshold power the large nonlinearity and small angular sensitivity must occur at the same phasematching orientation. It is more usual than not to find that crystal symmetry and optical orientation conspire to make the nonlinear coupling vanish in precisely the orientation which has the smallest angular sensitivity! Therefore, the next step in the screening procedure is to directly measure the phasematching properties and nonlinear coefficients in single crystals of the new materials.

Direct phasematching measurements (17) can be made on crystals as small as a few hundred microns, although we typically use crystals about 1 mm in cross section. This requires that the materials be recrystallized to the 1 mm range, if they are not already available in that size from the initial synthesis step. Nonetheless, this requires considerably less time and effort than growing the centimeter scale single crystals which would be required for traditional nonlinear coefficient measurements. As an example of the information generated by this technique, Figure 3 shows the results of direct phasematching measurements on a single crystal of dipotassium tartrate hemihydrate (DKT). The phasematching loci for type I doubling and tripling of 1.064 μm are plotted on a stereonet projection of a sphere, whose x, y and z axes correspond to the principal dielectric axes. The optic axes are designated by asterisks. Letters mark the positions of maximum harmonic generation intensity (maximum d_{eff}) while zeros mark the orientations where the effective nonlinear coefficient vanishes. The symmetry of the arrangement of the zeros and maxima is consistent with the monoclinic (2) symmetry of the crystal with the two-fold symmetry axis parallel to the high index (γ) axis. The values of the nonlinear coefficients and angular sensitivities at the marked positions are given in Table 1.

Table 1. Nonlinearity and angular sensitivity for type I doubling and tripling of 1.064 μm in dipotassium tartrate (DKT).

Position	θ	ϕ	$d_{\text{eff}}(\text{pm/V})$	$\beta(\text{cm}^{-1}/\text{mrad})$
2 ω I/a	+ 23°	$\pm 34^\circ$	0.14	3.7
2 ω I/b	- 10	± 48	0.13	4.6
3 ω I/a	+ 33	± 52	0.16	6.5
3 ω I/b	- 28	± 60	0.12	6.3

In DKT, as in other monoclinic crystals we have studied (17-18), the largest nonlinear coupling occurs at orientations which do not lie in the principal planes of the dielectric ellipsoid. Therefore, measurements which do not explore the entire phasematching locus could significantly underestimate the nonlinearity of these crystals. The value of the direct phasematching technique is that a complete "global" picture of the phasematching properties of even the lowest symmetry crystals is obtained in a straightforward way.

The sequence of measurements described in this section are designed to increase the efficiency of the screening process by sending a crystal on to a more involved stage of characterization only if it is likely to have the desired properties on the basis of the simpler measurements. The accuracy of each of the techniques is limited, so that in practice there is considerable chance that useful crystals will be rejected - and non-useful crystals will be selected - for further characterization. Nonetheless, these methods greatly enhance our ability to identify useful crystals before any serious crystal growth efforts are necessary.

The Chiral Organic Salt Strategy

For a wide variety of ionic and molecular crystals, the nonlinearity and other optical characteristics can be attributed to the electronic properties of molecules or molecular ions which compose the crystal (19-20). The bulk nonlinearity is approximated as the sum of the contributions of each molecular or ionic unit, weighted by geometric factors depending on the orientational arrangement of the units within the unit cell. Nature provides a variety of small noncentrosymmetric molecular units with electronic excitations at wavelengths shorter than 300 nm from which NLO crystals for laser fusion can be "built". Examples include the planar borate, carbonate, nitrate, carboxylate and guanadinium ions, certain molecular ions with nonbonding electrons such as iodate and bromate, and certain fluoride coordination groups involving d^0 ions such as titanium (IV) and niobium (V). It has long been understood that a crystal composed of these (or any other) units will not exhibit an appreciable nonlinear response unless it is noncentrosymmetric. In addition, the crystals which show the largest nonlinearity will be those in which the units are mutually oriented to give the largest net projections of the molecular hyperpolarizability tensor onto the bulk second order tensor of the crystal (20). In this context, crystal structures whose macroscopic nonlinearities express the largest fraction of the microscopic hyperpolarizability can be called "optimized".

Once a particular class of chemical compositions has been chosen for study, there are several strategies for finding crystals with noncentrosymmetric structures which allow the nonlinearity of the units to be expressed as a bulk nonlinearity. This includes "passive" approaches such as utilizing the crystallographic literature to identify known acentric phases with the desired chemical composition and exploring substitutional analogues, and "active" approaches which attempt to increase the probability that noncentrosymmetric crystals will be formed in completely new materials. While a number of "active" approaches have been

suggested (21-23), only the use of optically active enantiomers guarantees that the resulting crystal structure will be noncentrosymmetric.

We recognized (24-25) that many new NLO crystals which have properties favorable for ICF applications could be generated by a straightforward synthetic procedure, illustrated in Figure 4. These crystals consist of molecules which have at least one chiral center, and are optically active. The moieties attached to the chiral center are drawn from a large set of small charged or neutral fragments. At least one of these fragments should be a "harmonic generating unit", i.e. a noncentrosymmetric structure with delocalized bonding which will enhance the molecular hyperpolarizability. One of the fragments should be charged (this could be the harmonic generating unit itself, as in the case of the carboxylate anion.) This ionic chiral organic molecule can be co-crystallized with a variety of counterions, which might also be harmonic generating units themselves, to form a "chiral organic salt". It is also possible to have the chirality associated with a non-SHG active counterion, while the harmonic generating unit is non-chiral, e.g. formate ion co-crystallized with chiral amines. Often, such crystals will also incorporate one or more waters of hydration, depending on the conditions of crystallization. Finally, other chiral structures, such as those shown in Figure 5 could be utilized. It is clear that a wide variety of such crystals are possible, and that harmonic generating units which are much larger and more nonlinear than the ones we have listed could be used at the expense of a smaller transparency range, when the application warrants it.

The requirement that the molecule be charged, and the compounds be formed as salts is important for two reasons. First, at least for small molecules, it ensures water solubility. This is important for crystal growth, since it permits the techniques which allowed the scaling of KDP crystals to $30 \times 30 \times 60 \text{ cm}^3$ sizes to be applied without any fundamental changes. Second, the resulting crystals are at least partly ionic in character and hence have mechanical and thermal properties far superior to those of crystals stabilized by only VanderWaals or hydrogen bonding interactions. Third, generating different crystals by ion substitution is an important aspect of the strategy, as we will now argue.

The structure of a typical chiral organic salt is determined by several forces, including ionic, VanderWaals, and hydrogen bonding. Moreover, the molecules usually have some conformational flexibility. As a result, the actual crystal structure of a given compound cannot be predicted a priori. Therefore, we regard making a series of salts as a way of empirically exploring the "space" of structural arrangements which are possible for the harmonic generating units in such crystals. This, in turn, allows us to explore the space of resulting nonlinear and linear optical properties. When certain isovalent ionic substitutions are mild enough to cause no significant structural change (e.g. bromide for chloride) solid solutions can be used to fine tune the optical properties, similar to the way that solid solutions of the KDP isomorphs can be used to cover a range of noncritical wavelengths (2).

The use of salt formation to expand the number of crystals which contain a single molecular type was first applied by Meredith (26), and more recently by Marder et. al. (22). In the latter work, ionic interactions are used to offset dipolar interactions among achiral molecules, which enhances the probability that the resulting crystal will be noncentrosymmetric. In our case, of course, noncentrosymmetry is ensured by the chirality of the molecules involved. It is important to note that, within the picture we have presented, neither the assurance of noncentrosymmetry, nor the enhanced hyperpolarizability of the chiral molecule guarantees that the nonlinearity of any particular chiral organic salt crystal will be large. These properties simply ensure that each crystal so formed has an equal opportunity to express the molecular hyperpolarizability in an optimized way.

Whereas Figure 4 is intended to represent schematically the synthesis of an arbitrary chiral organic salt, in fact there already exist many commercially available chiral organic molecules

which fit the basic criteria. These are predominantly amino acids and alpha-hydroxy acids, and related derivatives. Nearly all of our studies so far have utilized these molecules, which we regard as models for the more general concept. (Not all of the crystals we studied were salts: some were zwitterionic or free base compounds where hydrogen bonding provides the dominant intermolecular forces.) It should be noted that, while the harmonic generating properties of a number of amino acid and hydroxy acid-containing crystals have been reported in the literature,(27) no systematic study of this general group of compounds has been previously attempted.

Statistical Model of the Search Process

Because the structure and optical properties of any particular compound cannot be predicted a priori, we have found it convenient to regard the search as a random process, sampling from a parent population with a fixed distribution of birefringences, nonlinearities, etc. To obtain an estimate of these distributions, we initially measured the powder SHG signals and refractive indices of more than 70 salts of commercially available amino and alpha-hydroxy acids and related compounds.(25) From the refractive indices, the principal birefringence and the optic angles of the crystals were computed. Approximate noncritical wavelengths were calculated for each crystal, using the empirical correlation between dispersion and refractive index discussed in the last section.

From this information, we have estimated(25) that between 0.5 and 1% of the chiral organic salts formed from amino acids and alpha-hydroxy acids have lower threshold powers than KDP for doubling or tripling 1.05 μm light. The probability P of finding such a crystal in a random sample of N crystals from the population of chiral organic salts is given by

$$P = 1 - (1 - p)^N$$

where p is the frequency of occurrence in the population. For $p = 0.005$, about 500 crystals must be examined to insure with 95% confidence that at least one low threshold crystal will be found. It is of some interest to compare this sample size with that which would be required if chirality were not utilized, assuming the same basic distributions of nonlinear and linear optical properties among the crystals of inorganic or achiral organic salts which were noncentrosymmetric. Figure 6 is a plot of N vs p for $P = 0.95$. Since only 30% of achiral organic crystals are noncentrosymmetric and about 20% of inorganic crystals, we would expect that the necessary sample size would increase to ~1000 and ~2500 crystals, respectively.

Strictly speaking, the empirical distributions given in reference 25 must be regarded as composites of subpopulations with varying types and densities of harmonic generating units because the molecules used to make the salts differed in size, type of unit, and number of units per molecule. Thus, for example, we would expect the distribution of powder intensities would be shifted towards larger values if we restricted the population to salts of chiral molecules having a higher ratio of harmonic generating units to total carbon atoms. Similarly, the distribution of noncritical wavelengths would be shifted towards longer wavelengths if we restricted the population to crystals containing heavier atoms, e.g. chloride, bromide or arsenate salts which raise the dispersion. To a large extent, chemical composition alone governs "average" optical properties such as the average refractive index and its dispersion. But chemical composition and molecular structure also determine the range of possible values of structure-dependent optical properties such as birefringence and nonlinearity in a set of crystals. Within this context, "molecular engineering" is regarded as a way of shifting the distribution to increase the probability of finding a crystal with particular properties.

Phasematching Properties of Chiral Organic Salts

To date, we have screened more than two hundred chiral organic salts and related compounds. Table 2 lists crystals which have noncritical wavelengths for frequency doubling

between 1.2 and 0.8 μm . The type of phasematching and the principal axis for noncritical phasematching are also listed. Because the crystals are biaxial, three noncritical wavelengths, corresponding to propagation down each of the three principal axes, are possible. For this reason several crystals appear more than once in this list. The value of the noncritical wavelength is accurate to about 0.02 μm . These compounds showed powder signals which were similar to, or larger than, KDP, but the value of the nonlinearity in the noncritical configuration is, in many cases unknown. Symmetry and optic orientation will often cause the nonlinearity to vanish identically. It should also be noted that hydrogen vibrational overtones are likely to cause very high absorption coefficients at wavelengths longer than 1 μm . Therefore, the utility of undeuterated crystals at those wavelengths is questionable even if they have large nonlinearities.

We have investigated the phasematching properties of many, but not all, of the crystals given in Table 2 using the direct measurement technique. In general, we have found that, as expected, most of the crystals do not have threshold powers lower than KDP for generating 0.527 or 0.351 μm light. Most often this occurs because, although the crystal has an orientation with larger nonlinearity than KDP, the angular sensitivity is also substantially larger and results in a larger threshold power. Conversely, most of the crystals we have examined which do have orientations with substantially lower angular sensitivities have vanishing or nearly vanishing nonlinear coefficients in those orientations. This is very often a consequence of the crystal symmetry and the optic orientation.

L-arginine fluoride (LAF) is an example of a low threshold power doubler we have discovered. Figure 7 shows the phasematching loci for frequency doubling 1.064 μm determined by direct phasematching measurements. The type I loci intersect the α - γ plane at $\pm 12^\circ$ from the α axis. At this orientation, the angular sensitivity is slightly smaller than that for type I doubling in KDP (4.3 vs. 4.9 $\text{cm}^{-1}/\text{mrad}$) but the effective nonlinearity is almost 4 times larger (0.98 vs. 0.26 pm/V). As a result, the threshold power for type I doubling is 16 times smaller for LAF, making it an attractive substitute for KDP in the polarization insensitive type I/type II THG schemes recently proposed for solid state fusion drivers.⁽⁴⁾

In LAF the low angular sensitivity orientation on the type I doubling locus is also the point of maximum d_{eff} . By contrast, consider the phasematching loci of N-acetyl tyrosine (NAT), described in Figure 8 and Table 3. Here both the type I and type II doubling loci have the same topology as the type I locus in LAF. In this case, however, the type I locus lies nearly 30° away from the α axis. Because the birefringence of this crystal is so large ($n_\gamma - n_\alpha = 0.14$) the resulting angular sensitivity at that orientation is 14 $\text{cm}^{-1}/\text{mrad}$ - almost a factor of three larger than KDP! The type I nonlinearity is not significantly larger than that of KDP, and the resulting threshold power is much higher. While the type II locus comes much closer to the noncritical orientation ($\pm 15^\circ$ from α), the nonlinear coupling is zero there because of symmetry.

L-arginine acetate (LAAc) is a low threshold power THG crystal which has emerged from our survey. The loci for type I SHG and type I THG of 1.064 μm light are shown in Figure 9. The type I THG locus intersects the α - β plane only a few degrees from the α axis. Because this is so close to the noncritical orientation, the angular sensitivity is very small. Unfortunately, the α axis coincides with the 2-fold symmetry axis in this monoclinic crystal, so the nonlinear coupling vanishes in this orientation. Nonetheless, two low threshold power orientations for type I tripling do exist in this crystal. The largest d_{eff} value (0.75 pm/V) is found in the β - γ plane, where the angular sensitivity is only 30% smaller than it is for type I THG in KDP (6.5 vs. 7.8 $\text{cm}^{-1}/\text{mrad}$). In addition, another (symmetry equivalent) pair of orientations exist with about 1/2 the angular sensitivity of KDP, and 20% higher nonlinearity (0.35 vs. 0.29 pm/V).

Table 3. Nonlinearity and angular sensitivity for type I and II doubling of 1.064 μm in N-Acetyl Tyrosine.

Position	θ	ϕ	$d_{\text{eff}}(\text{pm/V})$	$\beta(\text{cm}^{-1}/\text{mrad})$
2 ω I/A	± 6	43	0.18	15.0
2 ω I/B	0	28	0.28	13.8
2 ω I/C	0	- 28	0.41	13.8
2 ω I/D	± 10	- 41	0.34	14.9
2 ω II/A	± 14	20	0.22	4.5
2 ω II/B	0	58	0.18	6.9
2 ω II/C	0	- 58	0.12	6.9
2 ω II/D	± 15	22	0.10	4.5

Concluding Remarks

Once a low threshold power crystal has been identified, the long and arduous task of growing larger crystals remains. Crystals with dimensions of the order of 1 cm are necessary to evaluate many of the other properties which are important for ICF or other high power laser applications. Among these are optical absorption, stimulated Raman scattering (SRS) and stimulated Brillouin scattering (SBS) thresholds, and optical damage thresholds. This latter property differs from the others because, even at the fluences conceived of for ICF lasers, it is apparently governed by extrinsic factors such as impurities and defects. Thus, it is more a function of the crystal growth process than a property of the crystal itself. On the other hand, the SRS and SBS are serious parasitic nonlinear processes which are primarily governed by the composition and structure of the material itself. Until more information about these properties is obtained, it is by no means certain that the class of chiral organic salts and non-chiral analogues will be useful alternatives to KDP for fusion lasers even if crystals with substantially lower threshold powers are found.

The program reviewed in this paper can be regarded as a paradigm for any directed search for a new nonlinear crystal. Chemistry plays a key role in defining the space of chemical compositions which produce materials which meet the basic requirement of optical transparency for the desired application. The magnitude of the nonlinearity is ultimately limited by this, so that the pertinent issue is finding materials with the largest nonlinearity consistent with the transparency requirement. Basic structural criteria such as chirality, possibly augmented by crystallographic intuition, can be used to enhance the chances of finding noncentrosymmetric crystals and thus reduce the number of crystals which have to be examined. Among the set of crystals with "optimum" nonlinear coefficients will be a subset with near noncritical phasematching for the desired wavelengths. Ultimately, the final choice of a crystal from this set will depend on crystal growth and other issues.

Given the large number of nonlinear crystals which have been characterized since the phenomenon of harmonic generation was first observed, the search for a new crystal can almost always be regarded as a search for an alternative to some currently available "best choice". (For example, a suitable "baseline" material for diode laser frequency doubling might be potassium niobate.) Because of this, the value of finding an "improved" material can be accurately gauged in a relative sense, and compared to the cost of both the search and the

subsequent development of the material. To a large extent, the discovery and development of new crystals for harmonic generation now rests on such economic considerations.

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Figure Captions

Figure 1. The biaxial indicatrix, whose principal axes correspond to the refractive indices $n_\alpha \leq n_\beta \leq n_\gamma$. The optic axes are indicated by dashed lines and the optic angle is denoted $2V$. N is the principal birefringence.

Figure 2. Comparison of measured phasematching loci (solid curves) with those predicted by the approximate formula (dashed curves) for type I and II doubling in L-arginine fluoride. The asterisk marks the optic axis position.

Figure 3. Phasematching loci for type I SHG and THG of $1.064 \mu\text{m}$ in dipotassium tartrate (DKT).

Figure 4. General scheme for the synthesis of chiral organic salts.

Figure 5. Other possible structures for making chiral salts.

Figure 6. Sample sizes required to assure that a low threshold power crystal would be found among various crystal types.

Figure 7. Phasematching loci for type I and II doubling of $1.064 \mu\text{m}$ in L-arginine fluoride.

Figure 8. Phasematching loci for type I and II doubling of $1.064 \mu\text{m}$ in N-acetyl tyrosine.

Figure 9. Phasematching loci for type I tripling of $1.064 \mu\text{m}$ in L-arginine acetate.

Table 2. Crystals with non-critical wavelengths between 1.2 and 0.83 μm .

NCPM λ (μm)	I ^a powder	Compound	Axis ^b /	Type
1.228	1.6	N-ACETYL HIS	n1	II
1.175	0.5	L-ARG OXALATE	n1	I
1.155	1.0	HIS CF ₃ COOH	n1	II
1.149	0.6	L-ARG Cl H ₂ O	n1	I
1.14	0.3	L-ARG ACETATE	n1	II
1.133	0.5	HIS CH ₃ SO ₃ H	n1	II
1.123	0.8	MET MALIEATE	n3	II
1.066	0.5	NaH TARTRATE	n3	I
1.03	1.0	Cd LACTATE	n1	II
1.03	1.0	Cd LACTATE	n2	II
1.024	0.7	N-ACETYL PRO • H ₂ O	n1	I
1.012	1.0	HIS FLUOROBORATE	n1	II
1.003	1.2	N-ACETYL METHIONINE	n3	I
0.995	0.8	N-ACETYL TYROSINE	n1	II
0.959	0.8	MET NITRATE	n1	II
0.936	0.5	ALANINE CH ₃ SO ₃ H	n3	II
0.935	0.6	N-ACETYL ASN	n1	II
0.93	1.2	N-ACETYL METHIONINE	n2	II
0.926	1.4	L-ARG FLUORIDE	n1	I
0.923	0.3	L-ARG ACETATE	n2	II
0.923	0.6	N-ACETYL ASN	n3	I
0.91	1.0	N-ACETYL OH PRO	n3	II
0.906	0.8	NA L-VAL • NH ₃	n3	II
0.902	1.2	N-ACETYL METHIONINE	n1	I
0.885	1.9	Mg TARTRATE	n3	II
0.884	1.0	HIS ACETATE	n1	I
0.883	1.0	HIS CF ₃ COOH	n1	I
0.868	1.0	L-ARG CF ₃ COOH	n3	II
0.858	0.8	METHIONINE MALIEATE	n1	II
0.853	1.0	N-ACETYL OH PRO	n1	I
0.846	1.8	DIAMMONIUM TARTRATE	n3	II
0.837	1.0	ALANINE CH ₃ SO ₃ H	n2	II
0.831	1.9	MG TARTRATE	n2	II
0.831	0.5	HIS CH ₃ SO ₃ H	n1	I

^a Powder SHG signal relative to KDP

^b n1 = α , n2 = β , n3 = γ

Fig. 1

Fig. 2

Fig. 3

⊕ Counterion

⊕ Water of hydration (optional)

=

"Chiral organic salt"

Chiral Molecule (Charged) (A ≠ B ≠ D ≠ E)

Choose A - E from:

	Active	Inactive
Acid	$-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O}^- \end{array}$	$-\text{SO}_3^-$
Neut.	$-\text{NO}_2$	$-\text{OH} \quad -\text{H}$ $-\text{OR}$ $-\text{CH}_3\text{X}$
Base	$\begin{array}{c} \text{H} \quad \text{NH}_2 \\ \quad \\ -\text{NH} - \text{C} = \text{NH} \\ \\ \text{N} \\ / \quad \backslash \\ \text{C} = \text{H} \\ \\ \text{H} \end{array}$	$-\text{NH}_2$ $-\text{NRH}$

	Counterions	
Anions	F^- $\vdots$ I^-	$\text{R} - \text{COO}^-$ $\text{R} - \text{SO}_3^-$ PO_4^{3-} NO_3^- BF_4^-
	Li^+ $\vdots$ Tl^+ NH_4^+	Mg^{++} $\vdots$ Ba^{++} $\text{R} - \text{NH}_3^+$

Cyclic
compounds

Quaternary
ammonium
salts

Sulfonium
salts

QT-jt-u-11780

Fig. 5

Fig. 6

Fig. 7

Fig. 8

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