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ORGANIC NONLINEAR CRYSTALS AND
HIGH POWER FREQUENCY CONVERSION*

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Abstract

We are searching for new second- and third-harmonic generators among the salts of chiral organic acids and bases. We discuss the relevant properties of crystals from this group of compounds, including their nonlinear and phasematching characteristics, linear absorption, damage threshold and crystal growth. In addition, we summarize what is known concerning other nonlinear optical properties of these crystals, such as two-photon absorption, nonlinear refractive index, and stimulated Raman thresholds. A preliminary assessment is made of the potential of these materials for use in future high power, large aperture lasers such as those used for inertial confinement fusion experiments.

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INTRODUCTION

Can organic crystals be useful for frequency converting large aperture, high power lasers, such as those used in inertial confinement fusion (ICF)?¹ We have discovered several new second- and third-harmonic generators based on organic moieties. These compounds come from three broad, related categories: amino acid salts, salts of chiral carboxylic acids, and chiral zwitterions. In this paper, we will discuss the synthetic strategy for producing these compounds, their nonlinear and phasematching properties, and a number of other properties and considerations which will determine their ultimate usefulness. Many of the considerations relevant for ICF are also relevant to other kinds of applications of crystals used for frequency doubling or mixing.

The optimization of a material for a specific frequency conversion application is, in large part, determined by some simple scaling laws.² Each material can be characterized by a "threshold power" (P_{th}), which is roughly the smallest peak power a diffraction limited laser pulse must have to be doubled efficiently (> 50%) by that material. A diffraction limited beam with a peak power greater than or equal to P_{th} can be doubled with high efficiency regardless of how the beam aperture is changed by telescoping--as long as the crystal length is adjusted to compensate for the change in drive intensity. The threshold power is given by

$$P_{th} = \left(\frac{\lambda B}{C} \right)^2$$

where C is proportional to the nonlinear coupling d_{eff} , and is expressed in $\text{MM}^{-1/2}$ and β is the angular sensitivity ($\text{cm}^{-1}/\text{rad}$).

Thus, a small angular sensitivity can be as important an attribute as a large nonlinear coupling because a larger length of crystal can be used to convert a given laser beam. By this criterion (i.e. threshold power) any crystal which has a P_{th} lower than the power available for the intended application will convert efficiently.

However, all materials which satisfy a particular threshold power criterion are in no way equivalent or equally suitable in practice. This is because for each material one of several undesirable processes may limit the allowable drive intensity, and hence the minimum device aperture. This, in turn will limit the minimum crystal length sufficient for efficient conversion. Thus, aperture limiting processes give each material a characteristic minimum volume necessary to produce efficient frequency conversion without exceeding the threshold for these undesirable effects. The cost of producing the minimum volume of each material is an unambiguous figure of merit for distinguishing materials with similar threshold powers.

The major intensity (aperture) limiting processes are: optical damage, usually characterized by a damage fluence J_D ; two-photon absorption; stimulated Raman or Brillouin scattering, characterized by a gain coefficient g_s ; and self focusing or self phase modulation which depends on the nonlinear refractive index n_2 . The last three processes are usually a consequence of the intrinsic chemical composition of the material, but the damage threshold is more often determined by the presence of inclusions or defects incorporated during crystal growth.³

One other important material parameter is the linear absorption coefficient at the fundamental or harmonic wavelengths. Small amounts of linear absorption can become problematic when high average powers are

present.⁴ Clearly, for two materials with comparable absorption coefficients, the shorter crystal will absorb less total energy. In many cases, a smaller aperture will favor easier heat removal. Beyond these simple considerations, the avoidance of thermal problems depends on the thermal fracture limit and the coefficient of thermal dephasing of the material.⁴ These thermal properties will not be treated in this paper, but the optical absorption characteristics of the materials under consideration will be discussed.

CHIRAL ORGANIC SALTS

A large number of useful second harmonic generating crystals can be produced from molecular units composed of small, conjugated, ionic groups attached to chiral carbon centers. When these groups are intrinsically acentric, they have much larger hyperpolarizabilities than nonconjugated units, such as the phosphate ion. Examples of this kind of moiety are shown in Fig. 1. Crystals containing these molecules can be grown from aqueous solution as salts with various counterions, or as zwitterionic crystals. Molecular chirality guarantees that the crystals will be noncentrosymmetric, and most crystals which result from this approach fall into point groups 2 or 222. A large majority of the compounds we have examined have adequate birefringence for phase matched second- and third-harmonic generation of 1.064 μm light. Structural differences among these compounds lead to a variety of phase matching properties, e.g. noncritical phase-matching wavelengths. Some of the crystals have nonlinearities similar to or larger than that of urea. Moreover, as a group these ionic crystals are mechanically harder and more stable in air than urea.

In fact, a number of previously discovered harmonic generators belong to this class or are related to it, and a brief summary of these kinds of crystals is contained in Ref. 5. A survey of materials with threshold powers less than or equal to half the threshold power of potassium dihydrogen phosphate (KDP) for doubling or tripling $1.064\text{ }\mu\text{m}$ showed that nearly half the materials satisfying this criterion were in this general category.² However, our study represents the first systematic use of the general strategy outlined above to deliberately produce new materials in this class.

Table 1 gives the phase matching parameters for several crystals we have characterized recently: L-arginine phosphate (LAP), L-arginine fluoride (LAF), and diammonium tartrate (DAT). For comparison, the values for KDP are also given. Because the crystals from this class are biaxial, and usually monoclinic, traditional means of characterizing them (e.g. wedge and prism measurements⁶) would be very slow. However, we have recently developed a method of directly determining the phase matching properties of small crystals.⁷ With this method we can determine the maximum SHG efficiency of nonlinear crystals by exploring the entire phase-matching locus for any frequency doubling or mixing process of interest. Thus, even biaxial crystals can be quickly evaluated without the need for elaborate crystal growth efforts.

While chiral organic salts do not have nonlinearities as large as those found in certain high temperature oxides, such as barium metaborate,⁸ it is much easier to grow crystals in the sizes which will be necessary for future ICF lasers. Crystals of LAP have been grown by Cleveland Crystals Inc. under contract to LLNL to dimensions as large as $3\times 10\times 10\text{ cm}^3$. Crystals of DAT and LAF have been grown by simple

evaporation or cooling techniques to sizes as large as $2 \times 2 \times 1 \text{ cm}^3$ and $2 \times 1 \times 0.5 \text{ cm}^3$ respectively in our own laboratory.

The birefringence and nonlinear coefficients depend strongly on the structural details of each crystal. However, because the chemical moieties in these crystals are similar, we anticipate that many other properties which rely less critically on structural details will show marked regularities. In particular, the linear and two-photon absorption properties arise from the same kinds of spectroscopic transitions from crystal to crystal. Of course, it is possible that these properties will have strong polarization dependences which vary according to structure. In the remainder of this paper, we review the available information about potential aperture limiting processes in organic salts.

ONE PHOTON ABSORPTION

The ultraviolet edge is determined by strong $\pi \rightarrow \pi^*$ transitions associated with the small conjugated groups. This edge is generally at wavelengths lower than 250 nm for carboxylate or guanadyl groups, and may be somewhat redshifted for imidazolyl (Fig. 1).⁹ However, LAP exhibits a significant absorption feature (1-3 %/cm) in the region between 250 and 300 nm. This is probably due to $n \rightarrow \pi^*$ transitions. The wavelength of these transitions in carboxylic acids has been shown to depend significantly on the molecular structure,⁹ but very little information is known about their behavior in other kinds of organic salts.

In the near infrared, (0.9-1.5 μm) overtone absorptions of N-H, O-H, and C-H stretching vibrations can be quite strong. Extensively hydrogen bonded crystals such as LAP have overtone absorptions which lead to losses of 10-20%/cm at the Nd:YAG fundamental wavelength.^{10,11}

Deuteration can reduce this absorption to less than 1%/cm.⁷ C-H stretching overtones are significant at 0.910 and 1.2 μ m. These covalently bonded protons are not as easily replaced by deuterium, however.

TWO-PHOTON ABSORPTION

Almost no information is available concerning two photon absorption in organic salts. Simple symmetry arguments suggest that the same $\pi \rightarrow \pi^*$ transitions which determine the 1 photon UV edge are also significantly two photon active. (In fact, they must be if these transitions are to figure strongly in the $\chi^{(2)}$ response.) Thus, the "2-photon edge" is expected to begin around 400 nm, making the strength of such transitions an important issue for generating harmonics in the near ultraviolet.

NONLINEAR REFRACTIVE INDEX

The nonlinear index determines the threshold intensities for catastrophic self focusing. It correlates strongly with the size of the linear index and its dispersion. Measurements on LAP at LLNL indicate that n_2 is not significantly different than what would be predicted by refractive index scaling.¹² Table 2 contains n_2 data for LAP, KDP and potassium titanyl phosphate (KTP) for comparison.

STIMULATED RAMAN SCATTERING (SRS).

High frequency, narrow Raman resonances can lead to low thresholds for stimulated Raman scattering (SRS). Intense transverse SRS can cause significant energy loss or even physical damage to the nonlinear

crystals.¹³ Of primary concern in organic crystals are aliphatic C-H vibrations in the 2900 cm^{-1} region. These can have spontaneous Raman scattering intensities 2-3 times larger than other Raman active vibrations in these crystals, e.g. the carboxylate symmetric stretch at 1460 cm^{-1} .¹⁴ However, typical magnitudes of the aliphatic C-H mode scattering cross sections in these crystals are not known, nor have the linewidths been quantitatively documented. We may estimate the potential SRS gain by noting that the C-H modes (2858 cm^{-1}) in the aliphatic hydrocarbon decalin have an SRS gain coefficient of 0.7 cm/GW .¹³ (By comparison, the gain coefficient of the phosphate symmetric stretching mode in KDP is approximately 0.2 cm/GW .¹³) The relevance of this estimate is uncertain because the linewidths of such vibrations in crystals may be much smaller than those of liquid decalin. Nonetheless, it demonstrates the potential impact of these modes on SRS thresholds.

DAMAGE THRESHOLDS

Laser-induced damage can occur through a number of mechanisms, including thermal fracture from bulk absorption,⁴ local fracture at absorbing inclusions,³ or bulk photochemistry such as photorefractive damage or color center formation. For ICF applications the primary form of damage of concern is damage at absorbing inclusions.³

While the favorable bulk damage properties of organic materials are sometimes cited in the literature, little systematic evidence for high damage thresholds measured under well characterized conditions has been reported. However, damage tests of LAP and its deuterated analog LA*P have been done at LLNL and the results are shown in Table 3. For comparison, results obtained under the same conditions in KDP and KTP are

included. It is not known whether the high damage threshold of LAP vis à vis KDP is due to a smaller number of damaging inclusions or because the nature of the inclusions is different, or because LAP has better resistance to local fracture. Nonetheless, these results are convincing evidence that high damage thresholds can be found among organic crystals in the class we are examining. Although KTP is also capable of very high damage thresholds, scaling of this material to large sizes has not proven feasible.

CONCLUSIONS

Among the group of chiral ionic organic crystals are a significant number of materials which have moderately large nonlinearities (1-2 pm/V), favorable phase matching properties for generating light in the visible or near ultraviolet, and which grow easily into large, high optical quality crystals. The simple "molecular engineering" approach of attaching small, conjugated ionic groups to chiral carbon centers to produce new crystals of this type is far from exhausted. There is evidently no intrinsic constraint imposed by optical damage, and effects due to the nonlinear refractive index are not expected to be any worse in this class than in materials with similar linear refractive indices. Although limitations caused by two-photon absorption and stimulated Raman scattering have not yet been assessed with certainty, these materials hold considerable promise as candidates for use in high power frequency conversion.

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FIGURE CAPTIONS

1. Structures of some small conjugated groups which can be attached to chiral carbon centers (R^*) and cocrystallized with appropriate anions or cations to form second harmonic generators.

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Table 1. Properties of some ionic organic crystals for doubling 1.064 μm .

<u>Material</u>	<u>Type</u>	<u>$d_{\text{eff}}(\text{pm/V})^1$</u>	<u>$(\text{cm}^{-1}/\text{rad})$</u>	<u>$P_{\text{th}}(\text{MW})$</u>
LAP	I	1.6	6900	63
	II	1.5	4100	26
LAF	I	2.0	4900	21
	II	1.5	4100	26
DAT	I	0.86	5700	154
	II	0.59	2150	47
KDP	I	0.41^2	4900	500
	II	0.56	2500	70

1. Maximum d_{eff} for the given type.

2. Based on $d_{36} = 0.63 \text{ pm/V}$.

Table 2. Nonlinear refractive index (n_2) values for some frequency doubling crystals.

Crystal	n	$n_2(\times 10^{13} \text{ cm}^3/\text{erg})$
KDP	1.49	1.0 - 3.6 ¹
LAP	1.55	1.87 - 3.04 ²
KTP	1.77	2.5 - 5.7 ²

-
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Table 3. Damage thresholds of nonlinear crystals for 1 ns pulses at 1.064 μm .

<u>Crystal</u>	<u>Available size</u>	<u>$J_D(\text{J}/\text{cm}^2)$</u>
KDP	10x10x10 cm^3	5 ± 1
LAP	1x2x3	10 ± 2
KTP	0.5x0.5x0.5	13 ± 2

5054K

Carboxyl

Guanadyl

Histadyl

A-019-U-9295-1

Figure 1