Nonlinear Optical Phenomena in Oxides and Application to a Tunable Coherent Spectrometer*

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The material requirements for nonlinear interactions in crystal are reviewed with emphasis on the oxide crystals ADP, LiIO$_3$, and LiNbO$_3$. The nonlinearity, transparency, and phasematching properties of these three crystals allows efficient nonlinear interactions over a wide 0.22-4 μm spectral range. The advantages of nonlinear processes for generating tunable coherent radiation are illustrated by a tunable coherent spectrometer based on a 1.06 μm Nd:YAG pumped angle tuned LiNbO$_3$ parametric oscillator. The 1.4-4 μm parametric oscillator tuning range is extended by second harmonic generation in LiNbO$_3$, LiIO$_3$ and sum generation in ADP to 0.22 μm and by mixing in AgGaSe$_2$ and CdSe to 25 μm. The high energy computer controlled coherent spectrometer is now under construction.

I. Introduction

The first nonlinear optical experiment was conducted in an oxide material in 1961 when Franken et al. generated the second harmonic of a Ruby laser in SiO$_2$ (J). Since that early experiment nonlinear frequency conversion processes have become an integral part of laser technology. These processes include second harmonic generation, sum and difference frequency generation, and parametric oscillation. The frequency range available by nonlinear conversion processes extends from 0.200 μm in the uv to beyond 100 μm in the ir. It is interesting to note that nonlinear interactions in only three oxide materials, NH$_3$H$_2$PO$_4$(ADP), LiIO$_3$, and LiNbO$_3$ allow conversion and generation over the uv visible, and near ir part of this extended spectral range. In this paper, I consider the development and application of these oxide crystals to nonlinear optics. In addition to the material parameters, I discuss the application of these three oxide compounds to the generation of coherent radiation over the 0.22-4.0 μm spectral range. The unique properties of these crystals in nonlinear interactions allow one to conceive of a widely tunable coherent source. Such a tunable coherent spectrometer is presently being constructed and is described in the third part of this paper.

II. Linear and Nonlinear Optical Properties of Oxide Crystals

A. Material Requirements

Nonlinear crystals must satisfy four criteria if they are to be useful for nonlinear optical applications. These criteria are adequate nonlinearity, optical transparency, proper birefringence for phasematching, and sufficient resistance to optical damage by intense optical irradiation. These properties are briefly discussed in this section and are illustrated by descriptions of ADP, LiIO$_3$, and LiNbO$_3$.

1. Nonlinear susceptibility. In the early days of nonlinear optics adequate laser power was not always available to take full advantage of the potential conversion efficiency of a nonlinear crystal. Under those circumstances, the highest crystal nonlinearity was a very important factor. Since the late 1960s the situation has changed chiefly due to the avail-

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ability of well controlled high peak power laser sources at many wavelengths across the uv, visible, and ir spectral regions. Under present circumstances, the crystal nonlinearity becomes only one factor in determining the crystal’s potential for nonlinear applications. For example, if more than adequate laser power is available, then the nonlinear conversion efficiency is determined by the maximum incident intensity the crystal can withstand prior to the onset of optical damage.

The second harmonic generation conversion efficiency is given by (2, 3).

\[ \frac{I_{2\omega}}{I_\omega} = I^2 \frac{I^2}{I^2} \text{sinc}^2(\Delta k l/2), \]  

(1)

where \( I_{2\omega} \) and \( I_\omega \) are the second harmonic and fundamental intensities, \( I^2 I^2 \) is the conversion efficiency factor and

\[ \text{sinc}(\Delta k l/2) \equiv \frac{\sin(\Delta k l/2)}{(\Delta k l/2)} \]

is the phase velocity synchronism factor. For perfect phasematching \( \Delta k l = 0 \) and \( \text{sinc} (\Delta k l/2) = 1 \). Here \( \Delta k \) for second harmonic generation can be written as \( \Delta k = k_{2\omega} - 2k_\omega \) where \( |k| = (2\pi n l / l) \) is the wavevector.

In the low conversion efficiency limit the second harmonic generation efficiency, sum and difference generation efficiency, and parametric gain coefficient are equal. In the plane wave limit the conversion efficiency factor is (3, 4)

\[ I^2 I^2 = \frac{2\omega^2 |d_{\text{eff}}|^2 I^2}{n^2 c^3 \varepsilon_0} \]  

(2)

in MKS units. Here \( \omega \) is the fundamental frequency, \( l \) the crystal length, \( n \) the index of refraction \( (n_\omega = n_{2\omega} \text{ at phasematching}) \), \( c \) the velocity of light and \( \varepsilon_0 \) the permittivity of free space. The conversion efficiency varies as \( I_\omega \), the intensity of the fundamental wave, and as \( d_{\text{eff}}^2 \) the square of the effective nonlinear coefficient. This result holds in the plane wave focusing limit where the intensity \( I = P/A \) and the area \( A = \pi w^2/2 \) with \( w \) the Gaussian beam electric field radius.

From Eq. (2) it is evident that we can define a material figure of merit for nonlinear interactions in crystals by

\[ M = d^2/n^3. \]  

(3)

Figure 1 shows this figure of merit vs crystal transparency for a number of nonlinear crystals. Inspection of Fig. 1 shows that the oxide materials of interest, ADP, LiIO₃, and LiNbO₃ all have relatively low figure of merits when compared to semiconducting compounds. Fortunately, it is the conversion efficiency factor which is of interest in device applications, and in calculating \( I^2 I^2 \), the low material figure of merit for the oxide crystals is compensated by their extended violet and uv transparency range. This suggests that a comparison of \( I^2 I^2 \) is more useful. Figure 2 shows \( I^2 I^2 \) for nonlinear crystals vs transparency range. The second harmonic wavelength is noted by the tick marks and \( \lambda^2 \) is indicated. Figure 2 illustrates that whereas \( M \) varies over four orders of magnitude, \( I^2 I^2 \) is very closely within one order of magnitude for a very wide range of nonlinear crystals including the oxides. Furthermore, for reasonable intensi-
ties of less than 10 MW/cm\(^2\), we can expect \(r_2 \approx 1\) in most nonlinear materials for only 1 cm of interaction length. Clearly, parameters other than nonlinearity are important in determining the conversion efficiency for a nonlinear process.

Before discussing other material parameters let us return to Eq. (2) to consider the effective nonlinear coefficient \(d_{\text{eff}}\). The nonlinear susceptibility is described by an expansion of the polarization in terms of the electric field

\[ \chi = \epsilon_0 \left[ \chi^{(1)} E + \chi^{(2)} EE + \ldots \right], \]

where \(\chi^{(1)}\) is the linear susceptibility and \(\chi^{(2)}\) is the nonlinear susceptibility. In addition to satisfying an intrinsic permutation symmetry (5, 6) and Kleinman's symmetry (7), \(\chi^{(2)}\) must obey Neumann's Principle and satisfy crystal symmetry as well (8). It is customary to define a nonlinear coefficient \(d_{lm} = d_{jkr}\) where \(m\) runs from 1 to 6, in a reduced notation, such that

\[ \mathcal{P}(r, 2\omega) = \epsilon_0 \sum_{m=1}^{6} d_{lm}[E(r, \omega) E(\omega)]_m \times \exp[i2\chi^{(2)}(\omega)\cdot r], \]

with \(\chi^{(2)}(-2\omega, \omega, \omega) = 2d_{lm}(-2\omega, \omega, \omega)\) for second harmonic generation. The \(d\) tensors have the same symmetry as the piezoelectric tensors so that the nonzero components have been listed in tables (8–10).

As an example, the nonlinear \(d\) tensor for 42\(m\) point group to which KDP and its isomorphs belong has the components:

\[ \begin{align*}
\mathcal{P}_x &= \epsilon_0 2d_{14} E_y E_z \\
\mathcal{P}_y &= \epsilon_0 2d_{14} E_x E_z \\
\mathcal{P}_z &= \epsilon_0 2d_{36} E_x E_y.
\end{align*} \]

By Kleinman's symmetry \(d_{14} = d_{36}\) so that there is only one value for the nonlinear coefficient. A close look at the form of the tensor components shows that to maximize the nonlinear interaction in KDP type crystals, the field should propagate in a [110] direction. Furthermore, to achieve phasematching for negative uniaxial KDP (\(n_c < n_0\)) the propagation direction should be at an angle \(\theta\) with respect to the crystal optic axis such that \(n^{3\omega}(\theta) = n_0^\omega\). At this propagation direction, the projection of the polarization and electric fields leads to an effective nonlinear coefficient \(d_{\text{eff}} = d \sin \theta \sin 2\varphi\). Effective nonlinear coefficients have been listed for other crystal classes (11, 12). The effective nonlinear coefficient for LiIO\(_3\) is \(d_{\text{eff}} = d \sin \theta\). However, for LiNbO\(_3\) we find

\[ d_{\text{eff}} = d_{31} \sin \theta + d_{22} \cos \theta \sin 3\varphi. \]

A measurement for LiNbO\(_3\) shows that \(d_{31}\) and \(d_{22}\) have opposite signs so that \(d_{\text{eff}}\) is maximum for propagation in the negative \(yz\) quadrant. A consideration of \(d_{\text{eff}}\) is important for both the orientation of a nonlinear crystal and for the growth of crystals to satisfy particular phasematching requirements.

2. Transparency and optical quality. Known nonlinear materials have transparency ranges that extend from 0.220 \(\mu\)m in ADP through the infrared in a number of semiconductor compounds and beyond the restrahlen band into the far infrared in both oxide and semiconductor crystals. In general, the transparency range in a single material is limited by the band edge absorption at high frequencies and by two-phonon absorption at twice the restrahlen band at low frequencies. Materials are also transparent in the very low frequency range between
dc and the first crystal vibrational mode. Thus, nonlinear interactions may extend from the uv through the visible and ir to the far ir. In fact, only a few crystals having the proper birefringence and overlapping transparency ranges are needed to cover the entire extended frequency range. This is important because the growth of high optical quality nonlinear crystals is, in general, a difficult task. In addition, nonlinear crystals that can be grown well, are transparent, and have proper birefringence for phasematching are very rare among all known acentric crystals (14). For example, among 13,000 surveyed crystals, only 684 are uniaxial and phasematchable or 5.25%, and of these less than half have a nonlinearity greater than KDP and far fewer are amenable to crystal growth in high optical quality centimeter sizes.

The transmission loss in a nonlinear crystal reduces the SHG conversion efficiency by $e^{-\alpha_2 z + \alpha_1}$ where $\alpha_2$ and $\alpha_1$ are the loss per length at the second harmonic and fundamental waves. Thus, a 0.05 cm$^{-1}$ and 0.025 cm$^{-1}$ loss at 2$\omega$ and $\omega$ in a 1 cm long crystal reduces the SHG efficiency by 0.95 which is negligible. However, in a 5 cm crystal the same losses reduce the efficiency by 0.77, which is significant. High optical quality oxide materials have losses in the $10^{-3}$-$10^{-5}$ cm$^{-1}$ range, whereas semiconductor materials show much higher losses in the $1$-$10^{-2}$ cm$^{-1}$ range. The reduction of optical loss in nonlinear crystals is important if the nonlinear interaction is to proceed efficiently. It becomes even more important for operation of a parametric oscillator where the threshold pumping power and operating efficiency directly depend on the crystal and cavity losses.

Recently, intensity dependent losses have been recognized as important factors in the transparency of a crystal. At the short wavelength end of a material's transparency range, two-photon absorption may become the dominant loss mechanism even in a frequency range that is normally transparent to low intensity radiation. For example, at 10 MW/cm$^2$ the two-photon absorption in GaAs at 1.32 $\mu$m is 0.3 cm$^{-1}$, which is significant compared to the 0.05 cm$^{-1}$ normal absorption loss (15). This nonlinear absorption mechanism has also been observed in oxide nonlinear materials for intense pump radiation within the two-photon frequency range of the band edge. Thus for maximum efficiency pump wavelengths must be longer than the two-photon absorption edge of the nonlinear crystal although operation near the band edge is possible at lower efficiencies and pump intensities.

The two-photon absorption limit was in mind when pump wavelengths for the parametric gain calculations shown in Fig. 2 were chosen.

3. Birefringence and phasematching. For efficient nonlinear interactions phasematching must be achieved in the nonlinear crystal. As an example, SHG in cubic crystals that lack birefringence and thus are not phase-matchable, occurs only over a distance of one coherence length between 10 and 100 $\mu$m. By using birefringence to offset dispersion, the phasematched interaction may proceed over the full crystal length or approximately 1 cm. Since the SHG efficiency varies as $I^2$, phasematching increases the efficiency by at least $10^4$. The enormous improvement in nonlinear conversion efficiency due to phasematching makes phasematching essential in nonlinear crystals. Thus, if a crystal is nonlinear and transparent, it must still phasematch to be useful. Adequate birefringence for phasematching is the most restrictive requirement placed on a nonlinear crystal.

In conducting surveys for new nonlinear crystals, the crystal symmetry is determined by X-ray methods or by reference to existing tables (16). If the crystal is acentric and belongs to a point group that gives nonzero nonlinear coefficients for phasematching (17), then the crystal indices of refraction and birefringence must be determined. Fortunately, mineralogy texts and data collections are available (18) which list indices of refraction and birefringence for a large number of crystals. A comparison of the crystal birefringence against its index of refraction and similar quantities for known phasematchable crystals gives a quick indication of whether the potential nonlinear crystal has adequate birefringence for phasematching, Wemple (19), Wemple and DiDomenico (20), and Byer (14) have plotted
birefringence vs index of refraction for known nonlinear crystals to determine the minimum required birefringence for phasematching. Such plots are useful, since birefringence of a particular crystal cannot accurately be determined theoretically at this time.

Of course the above preliminary indications of possible phasematching in a new material must be carried a step further to determine the actual phasematching properties of a crystal. This is usually done by accurately measuring the crystal indices of refraction and fitting the results to an analytical expression which is useful for phasematching calculations. The measurement of crystal indices of refraction is tedious experimentally, especially in the ir, so that complete measurements have been made on only a few crystals (9, 10). The measurements must be accurate to 0.01 % for phasematching calculations to be made. For calculation purposes, the index values vs wavelength are usually expressed by a Sellmeier equation or modified Sellmeier equation. Once in this form, the phasematching expression for SHG $n_\theta \omega = n_\theta \omega (\theta)$ can be solved directly for the phasematching angle $\theta$. For three-frequency phasematching conditions, a small computer program is usually written to solve simultaneously the two equations $\omega_3 = \omega_2 + \omega_1$ and $k_3 = k_2 + k_1$, where $k = 2\pi m(\lambda)/\lambda$. Care must be taken in solving these equations since they may be double valued.

The LiNbO$_3$ parametric oscillator tuning curves shown in Fig. 3 were calculated in this manner using analytical expressions for the index of refraction given by Hobden and Warner (21).

Nonlinear crystals must also have a very uniform birefringence over the crystal length for efficient nonlinear conversion. In early stages of crystal growth birefringence variations may be a result of composition changes during growth. For example, early stoichiometrically grown LiNbO$_3$ crystals had birefringence variations which reduced their overall quality (22-25). The problem was fully solved by growth of LiNbO$_3$ from a congruent melt composition near a lithium to niobium ratio of 0.48 mole % (26, 27). The growth of LiNbO$_3$ crystals from a congruent melt plus improved optical tests for birefringence uni-

![Temperature tuned LiNbO$_3$ parametric oscillator tuning curves for various pump wavelengths of a doubled Nd: YAG Q-switched laser source.](image-url)
focusing, surface preparation, and dielectric breakdown. Thermal heating, in which the temperature rise of the material is proportional to the input pulse duration or deposited energy is a common damage mechanism in metals and highly absorbing materials. Semiconductors behave more like metals than dielectrics for this form of damage.

Damage thresholds for dielectric materials are generally much higher than for semiconductors. For example, sapphire damages near 25 GW/cm² for Q-switch pulse irradiation. Glass and Guenther (32) have reviewed damage studies in dielectrics. They point out that nonlinear materials show a marked decrease in damage threshold for phase-matched second harmonic generation. For example, LiIO₃ shows surface damage at 400 MW/cm² for 10 nsec pulses. When phase-matched it damages at 30 MW/cm² for the fundamental and 15 MW/cm² for the second harmonic. Similar results have been noted in LiNbO₃ and Ba₂Na₂Nb₅O₁₅.

Bass and Barrett (33) proposed a probabilistic model for laser induced damage based on an avalanche breakdown model. For this damage mechanism, the laser field acts as an ac analogue to dc dielectric breakdown. A laser power density of 10 GW/cm² corresponds to 4 x 10⁶ V/cm which is close to the measured dc dielectric breakdown fields near 30 x 10⁶ V/cm. Bass and Barrett (33) have presented the laser damage threshold in a probabilistic way such that the probability to induce damage is proportional to \( \exp(-K/E) \) where \( K \) is a constant and \( E \) is the rms optical field strength. Measured dielectric breakdown intensities lie near 25 GW/cm² for glasses and fused silica and between 2 and 4 GW/cm² for nonlinear crystals. It appears that if other damage mechanisms do not limit the laser intensity to lower levels, then laser induced dielectric breakdown determines the maximum incident intensity. Efforts to understand the mechanisms of laser induced damage have been increasing (34, 35). Hopefully these studies will lead to a better understanding of the material's damage intensity limits.

Fortunately, the damage intensity for most nonlinear materials lies between 10 MW/cm² and 1 GW/cm². Figure 2 then shows that nonlinear conversion efficiencies or parametric gains are high for crystal lengths on the order of 1 cm. The damage intensity does place a limit on the energy handling capabilities of nonlinear crystals. Thus, Q-switched laser pulses energies transmitted through 1 cm² area crystals are limited to 1–10 J. For most applications of nonlinear crystals, this is not a serious limit since the laser host medium and the nonlinear material damage at similar beam intensities.

B. Oxide Crystals

1. KDP and its isomorphs KDP, ADP, and their isomorphs are ferroelectric crystals (36) belonging to the 42m tetragonal point group above their Curie temperatures. The KDP crystals are transparent from 0.21 to 1.4 μm for the nondedeuterated and 0.21–1.7 μm for the deuterated material (37). ADP has a similar transparency range. KDP and its isomorphs are negative birefringent and are phase-matchable over most of their transparency range. Over small regions of wavelength the crystals 90° phasematch with temperature as the variable. For a complete reference to crystal indices of refraction see Milek and Wells (37), Bechmann and Kurtz (9), and Singh (10).

Because of the availability of large, high optical quality crystals, KDP and ADP were the subject of early nonlinear optical experiments by Miller (38, 39). Later Francois (40) and Bjorkholm and Siegman (41) made accurate cw measurements of ADP's nonlinearity. In addition, Bjorkholm (32) has made comparative nonlinear coefficient measurements of other crystals relative to KDP and ADP.

Parametric amplification was first reported by Wang and Racette (43) in ADP. Their report was closely followed by reports of parametric gain in KDP and ADP by Akhanov et al. (44). In 1966, Akhanov et al. (45) achieved parametric oscillation in KDP pumped by 0.53 μm from a KDP doubled Nd:Glass laser. That work was extended to the demonstration of parametric superfluorescence in a multipass traveling wave oscillator using ADP and KDP (46).

Recently, Yarborough and Massey (47) used the fourth harmonic of a Nd:YAG laser to generate high gain parametric
oscillation in ADP. This high gain oscillator generated 100 kW peak power and 10 mW average power output across the visible spectrum. Overall average power conversion from the 1.06 Nd:YAG source to the uv was 5.3% yielding an average power of 30 mW at 30 pps at 0.2662 \( \mu \text{m} \). The peak uv power was 200 kW and the power density at the ADP generator crystal was 750 MW/cm\(^2\).

KDP and ADP have played a significant role as efficient second harmonic generators for both cw and pulsed sources. For cw doubling ADP and KDP can be temperature tuned to the 90° phasematching condition over a limited range of fundamental wavelengths between 0.54 and 0.49 \( \mu \text{m} \) at temperatures between +60 and -80°C (48, 49). In particular ADP and KDP 90° phasematch for doubling 5145 \( \AA \) at -9.2 and -11.0°C. Other isomorphs of KDP 90° phasematch over different wavelength regions. For example, rubidium dihydrogen arsenate (RDA) 90° phasematches for doubling the 0.694 \( \mu \text{m} \) Ruby laser and cesium, dihydrogen arsenate (CDA) 90° phasematches for doubling 1.06 \( \mu \text{m} \) (50). Using 90° phasematched ADP, Dowley and Hodges (48) obtained up to 100 mW of 0.2573 \( \mu \text{m} \) in 1 msec pulses and 30–50 mW of cw power. The doubling was performed internal to an argon ion laser cavity to take advantage of the high circulating fields. The SHG efficiency was strongly dependent on crystal losses.

The uv transparency and phasematching characteristics of KDP isomorph crystals make them useful for uv generation by sum and second harmonic generation. Huth et al., (51), were the first to demonstrate this capability by externally doubling a dye laser source. Similarly, Yeung and Moore (52) and Sato (53) have generated tunable uv between 0.3044 and 0.3272 \( \mu \text{m} \) by summing a Ruby pumped dye laser and a Ruby laser. Wallace (54) reported an intracavity doubled dye laser that tunes between 0.2610 and 0.3150 \( \mu \text{m} \). This source uses a Q-switched internally doubled Nd:YAG laser as a pump source for the rhodamine 6G and sodium fluorescein dye laser. The KDP intracavity doubled dye laser produced 32 mW of average power at 0.2900 \( \mu \text{m} \) in a 2–3 cm\(^{-1}\) bandwidth. The conversion efficiency from input doubled Nd:YAG to uv power was 4.3%. At the 65° phasematching angle used for doubling the rhodamine 6G dye laser, ADP has a conversion efficiency to the second harmonic of 1% per 100 W of input power.

Recently, Massey (55) has shown that the fifth harmonic of 1.06 \( \mu \text{m} \) can be phasematched for sum generation in ADP. In addition, using a tunable source between 0.2460 and 0.3270 \( \mu \text{m} \) summed with 1.06 \( \mu \text{m} \) in ADP, wavelengths between 0.2500 and 0.2000 \( \mu \text{m} \) can be generated. This represents the shortest wavelengths that can be generated in a nonlinear crystal.

The optical quality and energy handling capability of KDP isomorphs is best illustrated by the work of Yarborough (56) and recently Falk and Ammann (57). Using a 10 pps, 1 J per pulse, Nd:YAG source, 45% efficient doubling to 0.5320 \( \mu \text{m} \) has been demonstrated in 90° phasematched 2 cm long CD*A crystal at a phasematching temperature of 103°C. The generated green output has been doubled again in ADP also 90° phasematched with 22% efficiency to generate 100 mJ pulses at 0.2660 \( \mu \text{m} \). The harmonic generation in both CD*A and ADP takes place without damage to the crystals. The output has been used to pump a dye laser with up to 50% conversion efficiency.

The high energy, high average power doubling experiments illustrate the optical quality of KDP and its isomorphs. In addition, the use of 90° phasematching for efficient second harmonic generation demonstrates its advantage in these experiments. Although KDP type crystals have not been utilized extensively in parametric oscillator studies, they play an important role in generating tunable uv radiation by second harmonic and sum generation of tunable visible sources.

2. LiNbO\(_3\). LiNbO\(_3\) is a ferroelectric material (58) with a Curie temperature approximately 40°C below its melting point of 1253°C. Since the recognition of the unique electro-optical (59) and nonlinear optical (60) properties of LiNbO\(_3\) in 1964, it has been extensively studied. The growth and physical
properties of LiNbO$_3$ have been discussed in a series of papers by Nassau et al. (61), and by Abrahams et al. (62). The electro-optical coefficients for LiNbO$_3$ have been measured by a number of workers (63–67) as have the indices of refraction (68, 69). A particularly useful form for the refractive indices, including temperature dependence, is given by Hobden and Warner (21).

Early work with LiNbO$_3$ showed two potentially troublesome optical properties: optically induced inhomogeneities in the refractive index (70–72) and growth dependent birefringent variations (22–25). The optically induced index inhomogeneities were found to be self annealing for crystal temperatures above approximately 180°C for visible radiation and 100°C for near ir radiation. Attempts to eliminate the induced index inhomogeneities have not been successful, so that LiNbO$_3$ parametric oscillators usually operate above 180°C. The growth dependent birefringent variations were eliminated by growth of LiNbO$_3$ from its congruent melting composition near a lithium to niobium ratio of 0.48 mole % (26, 27). The growth of LiNbO$_3$ crystals from a congruent melt plus improved optical quality tests (24–28) led to uniform high quality $a$ and $b$ axis single crystals of over 5 cm in length.

Ferroelectric LiNbO$_3$ has a large variation of birefringence with temperature. This allows SHG at 90° phasematching for fundamental wavelengths between 1 and 3.8 μm at temperature between 0 and 550°C. Conversely, LiNbO$_3$ 90° phasematches for parametric oscillation for a number of pump wavelengths and can be temperature tuned over a broad spectral region. Figure 3 shows the parametric oscillator tuning curves for various pump wavelengths of an internally doubled $Q$-switched Nd: YAG laser. These LiNbO$_3$ phasematching curves were calculated by using the Hobden and Warner (21) index of refraction expressions. Additional LiNbO$_3$ tuning curves, including angular dependence, are given by Harris (2) and Ammann et al. (73).

The internally doubled $Q$-switched Nd: YAG pumped LiNbO$_3$ parametric oscillator is the best developed parametric oscillator at this time. This system is described by Wallace (74). The Nd: YAG pump laser operates with an internal LiIO$_3$ doubling crystal, acousto-optic $Q$-switch and two Brewster angle prisms for wavelength selection. The combination of four doubled Nd: YAG pump wavelengths and temperature tuning allows the oscillator to cover the 0.54–3.65 μm spectral region.

Threshold for the LiNbO$_3$ parametric oscillator with a 5 cm long 90° phasematched crystal is typically between 300 and 600 W. The peak power conversion efficiency is near 50% for an oscillator operating a few times above the threshold. Due to the finite pump pulse width and oscillator build up time, the energy conversion efficiency is approximately 30%. However, much higher conversion efficiencies have been reported.

The parametric oscillator can be continuously tuned at between 2 and 10 cm$^{-1}$/min by scanning the oven temperature at 1°C/min. This tuning rate may be slow for some applications, but at 0.2 cm$^{-1}$ bandwidth for the resonant wave it is quite rapid tuning for a pulsed tunable source. There are now over 50 LiNbO$_3$ parametric oscillators in use. The properties of parametric oscillators are discussed in detail in reviews by Harris (2), Smith (75) and Byer (3).

LiNbO$_3$ is one of the highest quality nonlinear optical materials. Its use in parametric oscillators to generate tunable radiation over the 0.6–3.5 μm spectral range is a demonstration of its importance as a nonlinear material.

3. LiIO$_3$. In 1968, Kurtz and Perry (76) applied a technique based on the measurement of SHG of powders to the search for nonlinear materials. That search led to the evaluation of α-iodic acid (α-HIO$_3$) for phasematched second harmonic generation (77). Measurement of the nonlinearity of α-HIO$_3$ showed that it had a nonlinear coefficient approximately equal to that of LiNbO$_3$. The favorable nonlinear properties of α-HIO$_3$ led to consideration of other AIO$_3$ crystals (78). One of the first crystals considered was lithium iodate, LiIO$_3$. Its optical and nonlinear optical properties were studied by Nath and Haussuhl (79) and Nash et al. (80). The more
favorable optical quality of LiIO$_3$ compared to $\alpha$-HIO$_3$ has led to its use in a number of nonlinear applications spanning its entire transparency range from 0.35 to 5.5 $\mu$m.

LiIO$_3$ (point group 6) has a measured nonlinear coefficient slightly greater than that of LiNbO$_3$ (42, 81–83). Its indices of refraction and large birefringence ($An = 0.15$) have been measured as have phase-matching angles for various pump wavelengths. LiIO$_3$ phase-matches at 52° for doubling 0.6943 $\mu$m of a Ruby laser (84) and at 30° for doubling a 1.06 $\mu$m Nd:YAG laser.

LiIO$_3$ has proved particularly useful as a high optical quality nonlinear crystal for internal second harmonic generation of a Nd:YAG laser. For this application the laser mirrors are highly reflecting in the infrared but are transparent at the second harmonic. To obtain efficient doubling the laser operates Q-switched. In this mode, the LiIO$_3$ acts as a nonlinear output coupler and efficiently doubles the Nd:YAG. By operating with a prism in the laser cavity any one of 15 Nd:YAG laser lines can be selected and efficiently doubled by rotating the LiIO$_3$ to the phase-matching angle. In this way wavelengths at 0.473, 0.532, 0.579, and 0.659 $\mu$m can be generated. For example, peak powers of over 10 kW and average powers of greater than 1 W have been obtained from the internally doubled Nd:YAG laser source.

In 1970 Campillo and Tang (81) studied spontaneous parametric scattering in LiIO$_3$ and Dobrzhanskii et al. (85) carried out similar measurements in a $\alpha$-HIO$_2$. Shortly afterward, Goldberg (86) constructed a LiIO$_3$ parametric oscillator pumped with a Ruby laser and Izrailenko et al. (87) demonstrated an oscillator using LiIO$_3$ and $\alpha$-HIO$_3$ pumped by a doubled Nd:Glass laser.

The LiIO$_3$ oscillator can be compared with an off angle phase-matched LiNbO$_3$ oscillator. For equal loss and crystal lengths and $\theta = 50^\circ$ for LiNbO$_3$ the ratio of the oscillator gains is $R^2P(I_{1}Nd:O_{3})/R^2P(I:\text{LiIO}_3) \approx 3.6$. The LiIO$_3$ oscillator compares favorably to LiNbO$_3$ due to its higher damage intensity of 125 MW/cm$^2$ compared to approximately 80 MW/cm$^2$ for LiNbO$_3$. However, LiIO$_3$ does suffer from internal damage due to inclusions that may occur at lower intensities than for the surface damage.

Campillo (88) also externally doubled the LiIO$_3$ oscillator using an 8 mm LiIO$_3$ crystal cut at 21.4°. Figure 4 shows the phase-matching angles obtained in that experiment over a range of fundamental wavelengths between 1.1 and 1.8 $\mu$m. The second harmonic output at 100 W peak power tuned between 0.560 and 0.915 $\mu$m. Figure 4 also shows phase-matching data obtained by Herbst (89) in an internally doubled LiNbO$_3$ parametric oscillator and illustrates the phase-matching properties of LiIO$_3$ for SHG over a broad spectral region.

The ir transmission of LiIO$_3$ allows interactions out to 5.5 $\mu$m. Parametric oscillation is possible but not useful for idler wavelengths this far in the ir due to low gain. However, LiIO$_3$ does phase-match for mixing. Meltzer and Goldberg (90) have demonstrated mixing in LiIO$_3$ internal to a Ruby pumped dye laser. Output powers of 100 W were generated over the 4.1–5.2 $\mu$m region by mixing the Ruby source with the wavelengths from a DTTC dye laser. The spectral width of the dye laser was 6 $\AA$ in its 0.802–0.835 $\mu$m region. Although LiIO$_3$ is transparent and phase-matchable in the near ir spectral region, its low effective nonlinearity, due to the 19° phase-matching angle reduces its conversion efficiency to the point that other materials may prove more useful for infrared generation by mixing.
III. A Tunable Coherent Spectrometer

A. Growth of [01.4] LiNbO₃ Boules

Although present LiNbO₃ parametric oscillators are capable of tuning over a wide 0.6-3.5 μm spectral range, they have a number of disadvantages which preclude their use in a well controlled spectrometer. These include: temperature tuning and its disadvantages of slow thermal time constants and lack of direct control, low energy outputs, requirement for mirror changes to cover the full spectral range, and the requirement for visible pump wavelengths from a doubled Q-switched Nd: YAG laser source. The present oscillator does, however, have some significant advantages over other tunable sources. They include: wide tuning range in a single LiNbO₃ crystal, high gain and conversion efficiency, and narrow output bandwidths of less than 30 MHz by the use of internal etalon line narrowing techniques.

We have recently been able to overcome the above disadvantages of the LiNbO₃ parametric oscillator by employing LiNbO₃ crystals fabricated from LiNbO₃ boules grown in the [01.4] direction. The importance of LiNbO₃ boules grown along the [01.4] direction, which lies in the yz plane at 38° to the z axis, is in its application to an angle tuned 1.06 μm pumped high energy LiNbO₃ parametric oscillator described below. First, let me briefly discuss the growth procedure and results.

The requirement for a long (>5 cm) large diameter (>1 cm) high quality LiNbO₃ crystals with an axis direction at 47° to the optic axis for use in an angle tuned 1.06 μm pumped LiNbO₃ parametric oscillator, forced us to consider growing LiNbO₃ along other than the usual y axis direction. Typical y axis boules 8 cm in length by 1.5 cm cross section did not provide enough width to fabricate 47° oriented parametric oscillator crystals of adequate length. Although 1.06 μm parametric oscillators have operated (73, 91), they have not had adequate gain or conversion efficiency due to the limited length of available crystals. To overcome this problem we attempted to grow a boule along the [01.4] growth direction reported by Nassau et al. (61). This direction was chosen since it maximizes the effective nonlinear coefficient for LiNbO₃ and lies near the desired 47° propagation direction. Figure 5a shows a photograph of a typical [01.4] boule which is over 8 cm in length and 20 mm in diameter. Also shown is a fabricated crystal 5 cm in length and 10 mm diameter operating within a parametric oscillator cavity. The fabricated crystal is very high optical quality, being strain free, striation free and inclusion free over its full volume.

The [01.4] boule was grown in the standard fashion from an oriented (y axis polarity known) seed at the congruent composition. Following growth it was annealed for 24 hr and then poled by applying an electric field along the boule axis. The polarity of the poling field was chosen such that the boule axis was in the negative yz quadrant to maximize the effective nonlinear coefficient. To date 14 boules have been grown without difficulty with typical dimensions of 9 cm x 25 mm.

In addition to parametric oscillators, the material has been used to fabricate a c axis electro-optic modulator and 35° y-cut LiNbO₃ acoustic transducers. The high optical quality and ease of growth make the [01.4] growth direction preferable for obtaining optical grade LiNbO₃ material.

B. High Energy 1.06 μm Pumped LiNbO₃ Parametric Oscillator

The availability of high quality 5 cm long fabricated crystals in the 47° direction immediately led to the construction of a 1.06 μm pumped angle tuned LiNbO₃ parametric oscillator. The tuning curve for this oscillator is shown in Fig. 6. Figure 6 illustrates a number of potential advantages of this source. First, it is angle tuned which gives the possibility of rapid tuning with full computer control. Second, it has a greater than two-to-one tuning range 1.4 to beyond 4 μm. The oscillator generates two output frequencies within this range, the signal with $\lambda_s < 2.12$ μm and the idler with $\lambda_i > 2.12$ μm where 2.12 μm is the degeneracy wavelength. For operation as an oscillator the signal wave only is resonated. This leads to the third advantage of
Fig. 5a. Photograph of a [01.4] boule prior to poling

Fig. 5b. Photograph of a fabricated 47° parametric oscillator crystal 5 cm in length by 10 mm diam operating in a 1.06 μm pumped parametric oscillator.

this source. Only one set of mirrors are required to obtain the full tuning range of the oscillator so that the optical cavity can be assembled, aligned and permanently sealed. These advantages, along with the previously mentioned advantages of high gain and conversion efficiency, and potential operation at very narrow linewidths, make this device a very useful intermediate ir tunable source.

Experimentally we have verified the gain,
conversion efficiency and tuning of the 1.06 μm pumped parametric oscillator. The experiments were carried out using an electro-optic \( Q \)-switched 1.06 μm Nd:YAG laser operating at 20 mJ per pulse in a 20 nsec pulse at 10 pps in a TEM\(_{00}\) mode. The oscillator operated in a cavity formed by a 2-meter curvature and a flat mirror with the nonantireflection coated LiNbO\(_3\) crystal at room temperature. An energy conversion efficiency of greater than 30% was measured in preliminary experiments. The gain was adequate for oscillation from the crystal surfaces when the resonator was purposely misaligned.

These experiments have confirmed the high optical quality of the [01.4] grown LiNbO\(_3\) boules. The 15 mm diam fabricated crystals allow up to 2 J of 1.06 μm pump energy without exceeding the crystal damage intensity limit. To take advantage of the high energy handling capability of the present crystals, we are presently constructing a Nd:YAG oscillator amplifier system capable of 600 mJ output energy at 10 pps. Based on present laser technology, this 1.06 μm pump laser should operate at near 0.1% efficiency for over 10\(^7\) pulses or 270 hr at 10 pps rate before a flashlamp change is necessary. The high energy LiNbO\(_3\) parametric oscillator forms the heart of a widely tunable coherent spectrometer with an ultimate tuning range of 0.22 to beyond 25 μm.

C. Extended Frequency Coverage

The angle tuned LiNbO\(_3\) parametric oscillator can be looked at as the central tuning element in a computer controlled widely tunable coherent spectrometer. Its angle tuning and wide 1.5-4 μm tuning range make computer control through stepper motor driven angle stages practical. In addition, its high conversion efficiency and peak output power make further frequency doubling and mixing processes of the primary parametric oscillator wavelengths proceed efficiently. If these doubling and mixing crystals are also angle phasematched and computer controlled, then automatic continuous tuning over an extended range is feasible.

To extend the tuning range toward the visible, the oscillator output is doubled in LiNbO\(_3\), doubled again in LiIO\(_3\) and finally summed with 1.06 μm in ADP to reach 0.2200 μm. The doubling steps in LiNbO\(_3\) angle phasematch at near 65° to the optic axis has been experimentally measured to have a 52% energy and 70% peak power conversion efficiency. The generated output wavelength from this step covers the 0.75-1.5 μm spectral range.

LiIO\(_3\) phasematches for doubling the 0.75-1.5 μm wavelength range to give 0.375-0.75 μm output. Again, due to the high output powers available, the doubling step is efficient. The tuning range can be further extended into uv by second harmonic generation in ADP or KDP and by sum generation of 1.06 μm with wavelengths near 0.300 μm in ADP as recently demonstrated by Massey (55). Wavelengths as short as 0.220 μm can be generated in this manner.

The above frequency doubling steps are angle phasematched so that computer control is possible. The only optics required are polarizers and filters to isolate the generated wavelength of interest. The solid state oxide doubling crystals do not show deterioration with time which is a problem with dye lasers which also provide tunable radiation in this wavelength range.

The parametric oscillator tuning range can
be extended into the infrared by mixing in semiconductor crystals. For this frequency conversion step, the signal and idler of the parametric oscillator are simultaneously incident on the mixing crystal which generates the difference frequency. Phasematching is again achieved by control of the propagation angle within the nonlinear crystal. Mixing in the chalcopyrite AgGaSe₂ \( (92, 93) \) phasematches for generation of 3–18 \( \mu m \) wavelengths. Mixing in CdSe \( (94) \) phasematches to generate 10–25 \( \mu m \). Due to the lower optical quality of these semiconductor crystals as compared to the oxide materials, the photon conversion efficiency is expected to be near 10\%. However, mixing efficiencies as high as 35\% have been observed \( (94) \). The output power is further reduced by the Manley-Rowe frequency factor which accounts for the lower energy per photon at the generated infrared output wavelength.

Figure 7 illustrates the tuning range of the LiNbO₃ parametric oscillator as extended by second harmonic generation and mixing. Each tuning range shows the crystal used and the phasematching angle for the process. In all cases except the parametric oscillator, two crystals cut at different angles are required to angle phasematch over the full range. Based on the measured parametric oscillator efficiency and the LiNbO₃ doubling efficiency, and taking a conservative 30\% conversion efficiency as practical for the LiNbO₃ parametric oscillator source, we can estimate the expected output energy per pulse vs wavelength. Figure 8 shows such an estimate assuming a 300 mJ per pulse 1.06 \( \mu m \) pump source. The rapid decrease in energy per pulse in the infrared reflects the assumed 10\% mixing efficiency and the Manley-Rowe frequency ratio.

### IV. Conclusion

Nonlinear interactions in oxide crystals now allow efficient coherent frequency generation over a wide range of the uv, visible, and ir. Progress in the growth and perfection of three oxide crystals, LiNbO₃, LiIO₃, and ADP has opened a wavelength range from 0.22 to 4 \( \mu m \) to tunable coherent radiation. The progress in this direction is illustrated by the concept of a widely tunable coherent spectrometer.

Based on a LiNbO₃ parametric oscillator pumped at 1.06 \( \mu m \) and angle tuned over a 1.5–4 \( \mu m \) range, the computer controlled coherent spectrometer utilizes the basic advantages of nonlinear interactions in oxide materials. These include high conversion efficiency and tunability over a wide range of wavelengths.
efficiency, a wide tuning range for a single crystal, diffraction limited operation, unlimited crystal lifetime and well controlled angle phasematching. Without the combination of these features, unique to nonlinear interactions in crystals, one could not conceive of a computer controlled coherent spectrometer.

The high energy spectrometer is now under construction. Its PDP11/10 minicomputer will act to control the laser source and nonlinear crystal orientations, and will provide real time data handling and display. Initial applications of this unique source include optical pumping spectroscopy, nonlinear spectroscopy and remote air pollution measurements in the ir.

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